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of the
Environment

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PART A
AIR QUALITY RESEARCH

**NOVEMBER 30 &
DECEMBER 1, 1987**

**ROYAL YORK HOTEL
TORONTO, ONTARIO, CANADA**

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HAZARDOUS CONTAMINANTS
COORDINATION BRANCH
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PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 30 - DECEMBER 1, 1987

ROYAL YORK HOTEL

PART A

AIR QUALITY RESEARCH

Organized through the
RESEARCH ADVISORY COMMITTEE

Sponsored by
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INTRODUCTION

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations and companies.

The papers presented at the 1987 Technology Transfer Conference are included in five volumes of Conference Proceedings corresponding to the following sessions:

- Part A: Air Quality Research
- Part B: Water Quality Research
- Part C: Liquid & Solid Waste Research
- Part D: Analytical Methods
- Part E: Environmental Economics.

This part is a compilation of papers presented during Session B of the Conference.

For further information on any of the papers, the reader is kindly referred to the authors or to the Research Management Office at (416) 323-4574, 332-4573.

ACKNOWLEDGMENTS

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of Environment Ontario, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

SESSION A: AIR QUALITY RESEARCH

- A1 BIOLOGICAL AND CHEMICAL TESTING OF COKE OVEN EMISSIONS.**
N. Belson, A. Horton, and K. Shaw, G. Thomas,
Ontario Research Foundation, Mississauga,
Ontario.
- A2 HEALTH EFFECTS ON ASTHMATICS OF DAILY VARIATIONS IN EXPOSURE TO PARTICULATE MATTER.**
F. Silverman, P. Corey, A. Ayiomamitis
and H.R. Hosein, University of Toronto,
Toronto, Ontario.
- A3 ASSESSMENT OF TOXICITY OF DIGESTED AND INHALED HALOAROMATIC HYDROCARBONS.**
D.A. Clark and G. D. Sweeney, McMaster
University, Hamilton, Ontario.
- A4 DIRECT MEASUREMENTS OF GENETIC MUTATION AND ABERRATION RATES IN PULMONARY CELLS.**
J.A. Heddle, A. Bouch and D.B. Couch,
York University, Toronto, Ontario.
- A5 FIVE YEAR STUDY USING A MOBILE RAIN EXCLUSION CANOPY SYSTEM TO DETERMINE JOINT EFFECTS OF SIMULATED ACID RAIN AND OZONE ON THE GROWTH AND PHYSIOLOGY OF SUGAR MAPLE AND WHITE SPRUCE SEEDLINGS.**
A. Kuja and M. Dixon, Environment
Ontario, Brampton, Ontario.

- A6 MONITORING ENVIRONMENTAL GENOTOXICITY
USING SISTER CHROMATID EXCHANGES AND
MICRONUCLEUS INDUCTION IN HOUSE MICE.**
M. Petras, M. Vrzoc, K. Hill and C.
Helbing, Department of Biological
Sciences, University of Windsor, Windsor,
Ontario.
- A7 UTILIZATION OF ESTABLISHED AIR POLLUTION
MONITORING NETWORKS IN ONTARIO
FOLLOWING NUCLEAR INCIDENTS.**
J.A. Slade and S.H. Linauskas, Atomic
Energy of Canada Ltd., Chalk River,
Ontario.
- A8 CONTROL OF GASEOUS EMISSIONS AT THE
BROCK WEST LANDFILL SITE.**
R.E. Crysler, Trow Hydrology
Consultants Ltd., and L. Sweers,
Municipality of Metropolitan
Toronto (Works), Toronto, Ontario
Brampton, Ontario.
- A9 PASSIVE DEVICES FOR THE MEASUREMENT OF
AMBIENT SULPHUR DIOXIDE.**
D.B. Orr, J. C. Hipfner, W.H. Chan and
M.A. Lusi, Environment Ontario,
and J.E. Hunt, Concord Scientific Corp.,
Toronto, Ontario.
- A10 LABORATORY SCALE TESTING PROGRAM TO
DEVELOP UNDERSTANDING OF A PHOTO-
CHEMICAL FLUE GAS TREATMENT PROCESS.**
P. Fellin, K. Brice, C.S. Fung,
J.E. Hunt, Concord Scientific Corp.,
Downsview, Ontario.

- A11 TESTING A COMPREHENSIVE ACID DEPOSITION MODEL.**
P.K. Misra and R. Bloxam, Air Resources Branch, Environment Ontario, Toronto, Ontario.
- A12 AN EULERIAN MODEL OF LONG-RANGE TRANSPORT OF AIR POLLUTANTS AND ACID RAIN.**
Han-Ru Cho and J. V. Iribarne, Univeristy of Toronto, Toronto, Ontario.
- A13 SPATIAL AND TEMPORAL VARIABLITIES OF ACID RAIN LEVELS IN ONTARIO.**
E.A. McBean, M. Kompter, J. Donald, S. Donald and G. Farquhar, University of Waterloo, Waterloo, Ontario.
- A14 MODELLING THE PHOTOCHEMICAL DECOMPOSITION OF CHLORINATED PHENOLS BY SUNLIGHT.**
N. Bunce and J.S. Nakai, University of Guelph, Guelph, Ontario.
- A15 VECTOR SCORING SYSTEM FOR THE PRIORITIZATION OF CHEMICAL CONTAMINANTS.**
A.C. Socha, Environment Ontario, and R.F. Willes, CanTox Inc., Toronto, Ontario

- A16 RECEPTOR MODELLING OF AMBIENT AIR PARTICULATES AT EAST RIVERDALE AND TORONTO CONTROL SITES.**
R.E. Jervis, T.G. Pringle and A. Chan, University of Toronto, Toronto, Ontario.
- A17 DEVELOPMENT OF MULTIVARIATE ANALYSIS PROCEDURES FOR ONTARIO AIR QUALITY DATA.**
P.K. Hopke, Institute for Environmental Studies, University of Illinois at Urbana-Champaign, Urbana, Illinois.
- A18 CONTINUOUS MONITORING OF OPACITY, TOTAL HYDROCARBONS AND CARBON MONOXIDE IN AIR EMISSIONS FROM BIOMEDICAL WASTE INCINERATORS.**
G. Marson and V. Ozvacic, Air Resources Branch, Environment Ontario, Toronto, Ontario.
- AP1 DEVELOPMENT OF A TECHNIQUE FOR THE IDENTIFICATION OF AIRBORNE PARTICULATES.**
T. Kilner, Dept. of Math, Physics and Computer Science and S.G. Lea, Dept. of Applied Chemical and Biological Sciences, Ryerson Polytechnical Institute, Toronto, Ontario.
- AP2 THE EFFECT OF pH, ALUMINIUM AND DROUGHT ON SUGAR MAPLE SEEDLINGS.**
V. Timmer, M. Havas and T. Pajos, Faculty of Forestry, Institute for Environmental Studies, University of Toronto, Toronto, Ontario.

- AP3 CONCENTRATIONS OF PCDD AND PCDF IN SOIL FROM THE VICINITY OF A LARGE REFUSE INCINERATOR IN HAMILTON, ONTARIO.**
D. L. McLaughlin, R. G. Pearson, and
R.E. Clement, Environment Ontario,
Toronto, Ontario.
- AP4 DOSE RESPONSE FOR SELECTED ENVIRONMENTAL AIR POLLUTANTS: A STUDY ON RUNNERS.**
R.B. Urch, F. Silverman, P. Corey and
R.J. Shephard, Gage Research Institute,
Department of Medicine and Preventative
Medicine and Biostatistics and School
of Physical and Health Education,
University of Toronto, Toronto, Ontario
- AP5 STUDY TO DETERMINE THE PHYTOTOXICITY OF CALCIUM MAGNESIUM ACETATE (CMA) ON FRUIT TREES AND ORCHARD SOILS IN THE NIAGARA PENINSULA.**
R.G. Pearson and G.N. Vasiloff,
Environment Ontario, Toronto, Ontario
- AP6 ESTABLISHING VEGETATION ON EROSION-PRONE LANDFILL SLOPES IN ONTARIO.**
T.W. Hilditch and C.P. Hughes, Gartner
Lee Ltd., Markham, Ontario.
- AP7 EVALUATION OF A HI-VOL DENUDER SORBENT SAMPLING SCHEME FOR MEASUREMENTS OF POLYNUCLEAR AROMATIC HYDROCARBONS.**
G. Diamond, A. Szakolcai, J. Osborne
and S. Burns, Environment Ontario,
Toronto, Ontario.

**AP8 EFFECT OF FINE PARTICLES ON
RESPIRATORY HEALTH IN A COHORT OF
YOUNG PEOPLE.**

L.D. Pengelly, A.T. Kerigan and
C.H. Goldsmith, McMaster University,
Hamilton, Ontario.

**AP9 OUTDOOR SOUND LEVEL PREDICTION FOR
INDUSTRY, 1986**

T. Kelsall, Hatch Associates Ltd.,
Toronto, Ontario

**AP10 DEPOSITION OF HEAVY METALS AND
ACIDITY IN ONTARIO.**

N.W. Reid, D.B. Orr and M. A. Lusi,
Environment Ontario, Toronto, Ontario

BIOLOGICAL AND CHEMICAL TESTING OF COKE OVEN

EMISSIONS: PHASE II

by: N. Belson, A. Horton, K. Shaw & G. Thomas

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INTRODUCTION

The objective of the phase I study was to collect coke oven emission data for correlation with known human health effects. The study was designed to determine if a correlation exists between the benzene soluble fraction of total particulate material (BSFTPM) collected using low volume sampling methods and the dichloromethane soluble fraction of total particulate material (DSFTPM) collected using high volume sampling methods. In addition, the study was to determine if a correlation exists between the dichloromethane soluble fraction (DSF) and short term mutagenicity tests. This correlation could then be used as a marker to link the current study with existing occupational standards and epidemiological studies. To further strengthen this program chemical analysis of the dichloromethane soluble fraction (DSF) would be used to identify and quantify compounds, particularly polycyclic aromatic hydrocarbons (PAH's) and permit an assessment of relationships with known health effects.

The sampling protocol involved direct sampling of a coke oven throughout the coking cycle by means of a hole drilled through the coke oven lid (LID samples). Concurrently, sampling was also performed on the coke oven top side (COTS samples) during the complete coking cycle. The sampling protocols provided sample sets from each location which consisted of a High Volume [filter plus polyurethane foam (PUF) back-up plug] sample and a Low Volume (filter) sample.

The phase I study showed that a good correlation exists between the BSFTPM collected using low volume sampling methods and the DSFTPM collected high volume sampling methods. The study also showed a positive relationship between the DSFTPM of coke oven emissions and mutagenicity.

The mutagenicity results showed that the DSFTPM from coke oven emissions is positive and mutagenic for Salmonella strain TA-98 in the presence of metabolic activation. The study further showed that the DSF induced Sister Chromatid Exchanges in Chinese Hamster Ovary Cells (SCE-CHO) in the presence and absence of the metabolic activation. The highly volatile material collected on PUF's was also positive and mutagenic for Salmonella strains TA-98 and TA-1537 with metabolic activation.

Chemical analysis indicated that most of the compounds present in the DSF, that were gas chromatographable were polycyclic aromatic hydrocarbons. They consisted of unsubstituted PAH's, alkylated derivatives and nitrogen containing aza-arene type compounds. The study further showed that the concentration of the major PAH's was consistent throughout the coking cycle and that the same compounds were present in the top side samples. The PUF samples which collected the pass through gaseous components were shown to be mostly low molecular weight PAH type compounds.

OBJECTIVE (Phase II)

The objective was to utilize selected samples from those collected and analyzed in Phase I to further define and quantify the chemical composition of COE and relate these findings to the mutagenicity of the unfractionated samples. This was to be achieved by utilizing a fractionation scheme in order to separate the complex mixtures into well defined sub-fractions to better isolate the mutagenicity and better define the chemistry both qualitatively (identification) and quantitatively.

EXPERIMENTAL

Storage Effects

Before proceeding with the fractionation scheme of the selected SOF, it was necessary to check out the possible effects of storage (1-1/2 years) on the Ames bioassay response to the original samples. A study was conducted using COTS-SOF filter #105. This sample permitted the testing of different storage conditions for their effect on the Ames bioassay. These different storage conditions were:

- Dichloromethane (DCM)-SOF in the fridge
- DMSO (solvent exchange) frozen at -18°C
- A filter (#106) collected at the same time as filter #105 had been stored as an unextracted filter. Filter #106 was extracted with DCM and then treated in the same manner as the #105 extract prior to conducting the Ames test.

The bioassay results for these COTS samples that had been retained under different storage conditions did not show any significant increase or decrease in sample mutagenicity. A similar bioassay result was observed for a LID sample that had been tested in Phase I and retested in Phase II along with the fractions.

Fractionation

A schematic of the fractionation procedure used in the study is shown in Figure 1. A standard mixture containing seven (7) model compounds was processed through the alumina column in order to optimize the chromatographic conditions to obtain the desired separation amongst the specific compound types. The seven model compounds used were eicosane and octadecane (hydrocarbons); acridine and carbazole (aza-arenes); phenanthrene, pyrene and benzo(a)pyrene (parent PAH). Good separation conditions were obtained for the three classes of model compounds.

The intent when following the proposed fractionation scheme is to collect four (4) fractions from the alumina column. Each of these fractions was analyzed by GC/MSD for chemical characterization. In addition, each of the fractions was subjected to an Ames bioassay.

Fractionation of COE-SOF

Four (4) types of COE-SOF have been processed through the fractionation scheme. They are:

- (a) LID - SOF
- (b) COTS- SOF
- (c) LID - PUF - SOF
- (d) COTS- PUF - SOF

The collected fractions from the four different sample types have been subjected to the Ames bioassay and detailed chemical analysis.

Biological Testing

The bioassay employed was the Ames Salmonella mutagenicity assay. Sample preparation for testing involved the selection of a suitable aliquot of the SDF calculated to contain sufficient material for the test assay. The material was transferred to a small tray and allowed to dry at room temperature in a fume hood. The weight of the dry extract was determined. The extract was dissolved in a suitable volume of dimethylsulphoxide (DMSO) to give a concentration of 10,000µg/mL.

Chemical Testing

Aliquots (1 mL) of the SDFs were sealed in hypo-vials, labelled and stored at 4°C prior to chemical analysis. For analysis a suitable aliquot (2µl) of the extract was injected into a gas chromatograph-mass selective detector (GC-MSD) system. The system used was:

Equipment:	Hewlett-Packard Model 5890 gas chromatograph with capillary direct interface to Model 5970B Mass Selective Detector: with ChemStation
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Gas Chromatographic Conditions:

Column	: 60 m x 0.32 mm J & W DB-5
Column Temperature	: 50°C to 300°C at 10°C/min
Injector	: Splitless/Autosampler
Flow Rate	: Approx. 1 mL/min Helium
Interface Temperature	: 275°C

Mass Spectrometer Conditions:

Acquisition:	: Full scan acquisition with use of extracted ion current profiles for identification and quantitation
Mass Range	: 35-300 amu
Scans/seconds	: 3

Data Archiving:

Tape Drive	: HP 9144 cartridge tape drive used for archival storage of data
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RESULTS

A comparison of the fractions collected in terms of percent of the original extract for the different sample types is presented in Figure 2. A summary of the biological test results for the various fractions is presented in Table 1 as either positive/negative or not tested.

Data for each of the fractions from the respective LID and COTS extracts in which the fraction weight is expressed as mg or $\mu\text{g}/\text{m}^3$ is presented in Tables 2 and 3. In addition these tables report the mutagenic data in terms of calculated specific activities (revertants/ μg). The specific activity is defined as the slope of the linear portion of the dose response curve.

The chemical analysis of the various fractions has resulted in the tentative identification of approximately 80 chemical compounds the majority of which are PAH. The distribution of the PAH amongst the various fractions was as expected with the majority of the parent PAH plus alkylated species present in fraction #2 and the aza-arene type PAH species present in fraction #3. The tentative identifications of the parent + alkylated PAH are summarized in Table 4. This table contains a listing of the compound types together with formulae and molecular weights for the respective compounds identified. Similarly, the tentative identifications for the aza-arene compounds are summarized in Table 5. This table contains a listing of the compound types together with formulae and molecular weights for the respective compounds identified.

In the case of the PUF-SOF fractions a major preponderance of the low molecular weight (128-202) PAH components was evident. The whole spectrum of PAH molecular weights (128-278) with a preponderance of the middle to high range (178-278) was evident in the filter - SOFs.

Actual weights for individual compounds expressed as $\mu\text{g}/\text{m}^3$ are being calculated for the respective fractions under investigation. These results together with their implication with respect to the biological data will be discussed during the presentation.

FIGURE 1

FRACTIONATION
SCHEME

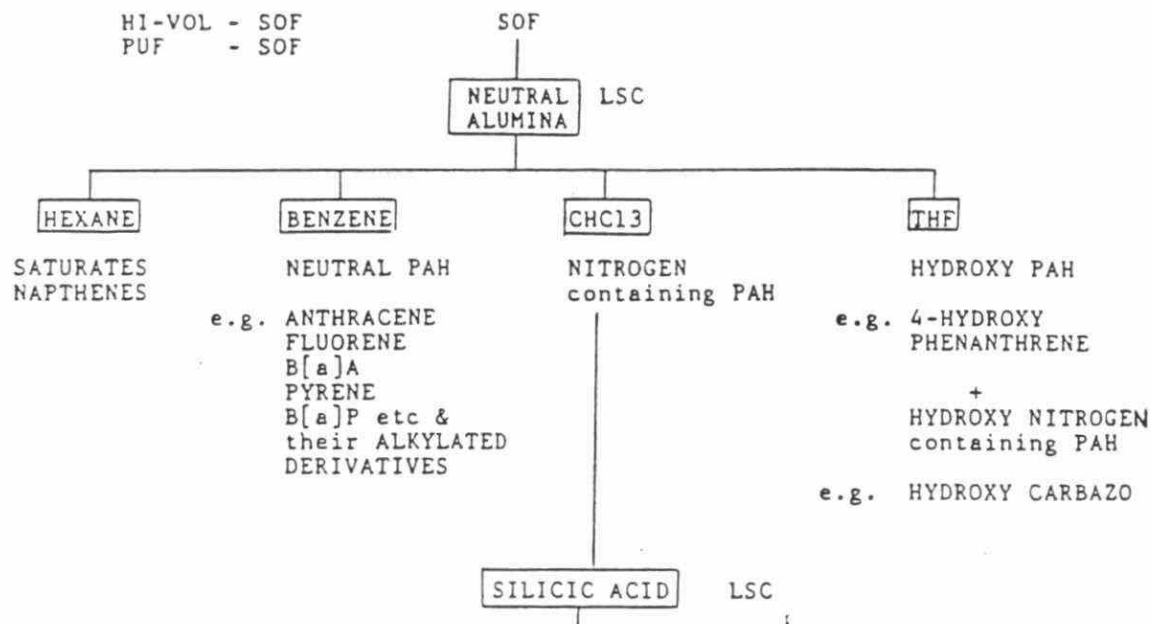


FIGURE 2

Comparison of Fractions

Mill #1 and Mill #2

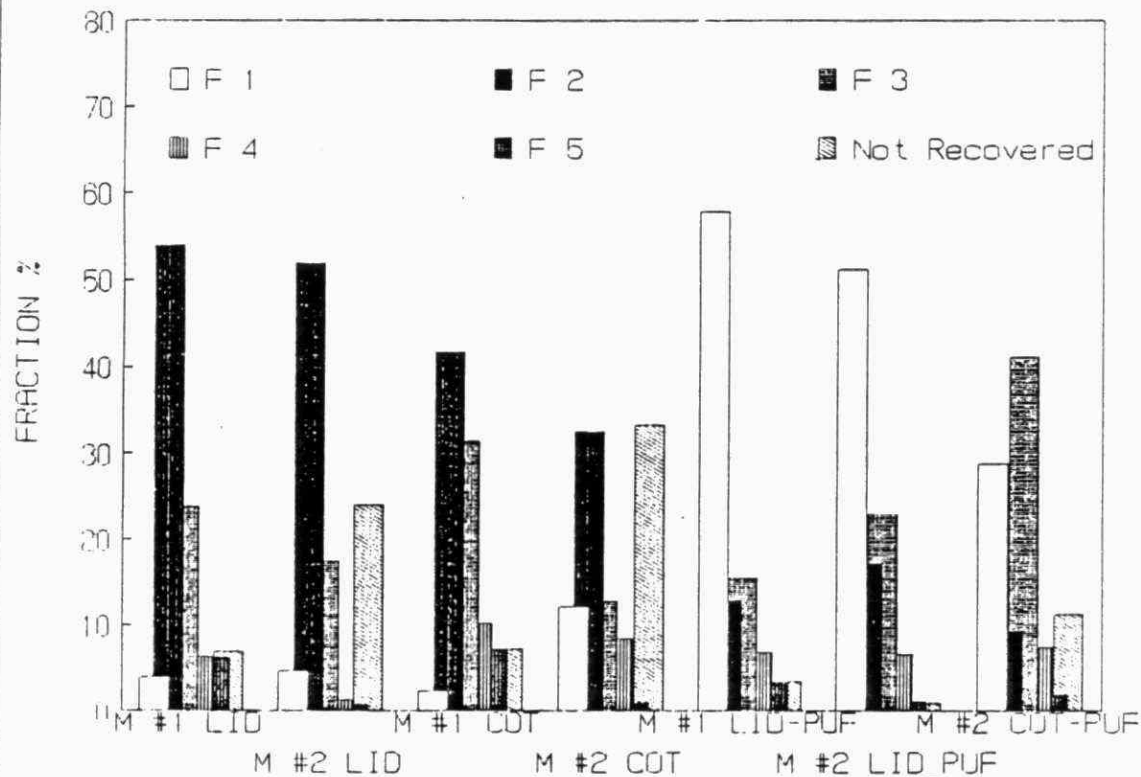


TABLE 1

FRACTION MUTAGENICITY

MILL # 1 / MILL # 2

FRACTION	LID	COT	LID-PUF	COT-PUF
F0	+/+	+/+	+/ND	ND/ND
F1	-/-	-/-	-/-	ND/-
F2	+/+	+/-	+/+	ND/-
F3	+/+	+/+	+/+	ND/-
F4	+/+	+/-	+/-	ND/-
F5	+/+	+/-	ND/ND	ND/ND

+ = POSITIVE

- = NEGATIVE

ND NOT DONE

TABLE 2

FRACTION MUTAGENICITY

MILL # 1 8 Hr LID

FRACTION	WEIGHT Mg/M3	SPECIFIC ACTIVITY	
		Rev/ug W/O	Rev/ug W
F0	518	3.9	19.3
F1	20	0.0	0.0
F2	280	1.4	23.7
F3	123	0.4	2.0
F4	27	0.6	1.3
F5	32	1.8	3.9
F6	36	ND	ND

ND - NOT DONE F6 NOT RECOVERED

FRACTION MUTAGENICITY

MILL # 2 8 Hr LID

FRACTION	WEIGHT Mg/M3	SPECIFIC ACTIVITY	
		Rev/ug W/O	Rev/ug W
F0	299	4.8	24.9
F1	14	0.0	0.0
F2	155	3.1	25.1
F3	52	0.7	10.0
F4	4	18.1	17.0
F5	2	ND	3.4
F6	72	ND	ND

ND - NOT DONE F6 NOT RECOVERED

TABLE 3

FRACTION MUTAGENICITY

MILL # 1 COT

FRACTION	WEIGHT ug/M3	SPECIFIC ACTIVITY	
		Rev/ug W/O	Rev/ug W
F0	540	0.9	14.0
F1	12	0.0	0.0
F2	226	1.9	15.9
F3	170	3.0	5.9
F4	55	1.3	1.7
F5	38	1.2	1.9
F6	39	ND	ND

ND - NOT DONE F6 NOT RECOVERED

FRACTION MUTAGENICITY

MILL # 2 COT

FRACTION	WEIGHT ug/M3	SPECIFIC ACTIVITY	
		Rev/ug W/O	Rev/ug W
F0	2900	0.0	10.8
F1	348	0.0	0.0
F2	945	0.0	0.0
F3	371	0.0	6.5
F4	244	0.0	0.0
F5	26	0.0	0.0
F6	966	ND	ND

ND - NOT DONE F6 NOT RECOVERED

TABLE 4

M.Wt.	Compound	Formula
94	Toluene	C_7H_8
134	Benzothiophene	$C_{10}H_{14}$
128	Naphthalene	$C_{10}H_8$
142	C_1 -alkyl	$C_{11}H_{10}$
156	C_2 -alkyl	$C_{12}H_{12}$
154	Acenaphthene	$C_{12}H_{10}$
152	Acenaphthylene	$C_{12}H_8$
168	Dibenzofuran	$C_{12}H_{10}O$
182	C_1 -alkyl	$C_{13}H_{10}O$
166	Fluorene	$C_{13}H_{10}$
178	Phenanthrene	$C_{14}H_{10}$
178	Anthracene	$C_{14}H_{10}$
192	C_1 -alkyl	$C_{15}H_{12}$
206	C_2 -alkyl	$C_{16}H_{14}$
184	Dibenzothiophene	$C_{12}H_8S$
190	4H-cyclopenta[def]phenanthrene	$C_{15}H_{10}$
202	Pyrene	$C_{16}H_{10}$
202	Fluoranthene	$C_{16}H_{10}$
216	C_1 -alkyl	$C_{17}H_{12}$
216	Benzofluorene	$C_{17}H_{12}$
228	Benz[a]anthracene	$C_{18}H_{12}$
228	Chrysene	$C_{18}H_{12}$
228	Triphenylene	$C_{18}H_{12}$

Continued . .

TABLE 4

M.Wt.	Compound	Formula
Continued . .		
242	C ₁ -alkyl	
226	Benzo[ghi]fluoranthene	C ₁₈ H ₁₀
240	C ₁ -alkyl	
252	Benzo[b]fluoranthene	C ₂₀ H ₁₂
252	Benzo[j]fluoranthene	C ₂₀ H ₁₂
252	Benzo[k]fluoranthene	C ₂₀ H ₁₂
252	Benzo[a]pyrene	C ₂₀ H ₁₂
252	Benzo[e]pyrene	C ₂₀ H ₁₂
252	Perylene	C ₂₀ H ₁₂
266	C ₁ -alkyl	C ₂₁ H ₁₄
266	Dibenzo[ac]fluorene	C ₂₁ H ₁₄
276	Indeno[1,2,3,cd]pyrene	C ₂₂ H ₁₂
276	Benzo[ghi]perylene	C ₂₂ H ₁₂
276	Anthanthrene	C ₂₂ H ₁₂
278	dibenz[ac]anthracene	C ₂₂ H ₁₄
278	dibenz[ah]anthracene	C ₂₂ H ₁₄
278	benzo[b]chrysene	C ₂₂ H ₁₄
278	Picene	C ₂₂ H ₁₄
300	(Coronene	C ₂₄ H ₁₂
	(Dibenzo[ghi,per]perylene	
302	Dibenzo[e,l]pyrene	C ₂₄ H ₁₄

Continued . .

TABLE 5

M.Wt.	Compound	Formula
129	Quinoline	C_9H_7N
129	Isoquinoline	C_9H_7N
143	C_1 -quinoline	$C_{10}H_9N$
157	C_2 -quinoline	$C_{11}H_{11}N$
171	C_3 -quinoline	$C_{12}H_{13}N$
167	(Azafluorene (Carbazole	$C_{12}H_9N$
169	Azadibenzofuran	$C_{12}H_{11}N$
169	C_1 -aza-acenaphthene or diphenyl	$C_{12}H_{11}N$
179	2,3-benzoquinoline 3,4-benzoquinoline 5,6-benzoquinoline (7,8-benzoquinoline (Acridine	$C_{13}H_9N$
181	C_1 -azafluorene	$C_{13}H_{11}N$
183	C_1 -azadibenzofuran C_2 -aza-acenaphthene or diphenyl	$C_{13}H_{13}N$
185	Azadibenzothiophene	$C_{11}H_7NS$
191	Phenanthro[bcd]pyrrole	$C_{14}H_9N$
193	C_1 -benzoquinoline	$C_{14}H_{11}N$
199	C_1 -azadibenzothiophene	$C_{12}H_9NS$
203	Azafluoranthene/pyrene	$C_{15}H_9N$
205	C_1 -aza-cyclopenteno[def] phenanthrene	$C_{15}H_{11}N$
207	C_2 -benzoquinoline	$C_{15}H_{13}N$

Continued . .

TABLE 5

M.Wt.	Compound	Formula
Continued . .		
217	C ₁ -azafluoranthene/pyrene	C ₁₆ H ₁₁ N
229	3,4-Benzacridine	C ₁₇ H ₁₁ N
229	Dibenzoquinoline	C ₁₇ H ₁₁ N
253	Azabenzofluoranthene/pyrene	C ₁₉ H ₁₁ N
267	Dibenzo[ai]carbazole	C ₂₀ H ₁₃ N
279	Dibenz[ah]acridine	C ₂₁ H ₁₃ N
168	Azacarbazole	C ₁₁ H ₈ N ₂
194	C ₁ -azaphenanthrene	C ₁₃ H ₁₀ N ₂

HEALTH EFFECTS ON ASTHMATICS OF DAILY
VARIATIONS IN EXPOSURE TO PARTICULATE MATTER

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ABSTRACT

The health risk of low level air pollution exposure is still uncertain. Vertical and horizontal differences in air pollution exist and outdoor air differs substantially from indoor air. Thus levels of air pollution measured at fixed outdoor sites may not reflect levels actually inhaled by an individual, i.e. "personal exposure". Effects documented using severe response variables tend to ignore minor fluctuations in disease, e.g. asthma.

In this study, exposure was assessed by both personal monitoring and at a fixed air pollution monitoring site in downtown Toronto, to examine the relative strengths of the two estimates of exposure as demonstrated by their association with measures of health effects (pulmonary function). Small multipollutant samplers for nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and particulate matter were carried by volunteer asthmatic subjects (P), and simultaneously a sampler of the same design operated at a downtown Toronto air pollution monitoring station (GMOE). Subjects were each tested on up to 20 days in both summer ($n=10$) and winter ($n=10$); pulmonary function (spirometry) was assessed at the beginning and end of each monitoring day.

A longitudinal analysis, within individuals, of the relationship between pulmonary function and particulate matter, revealed a season effect when the personal exposure monitoring data (P) were used. This was not observed when

the exposure data from the fixed-site (GMOE) were used in the analysis. Using a cross-sectional analysis correlating mean pulmonary function with mean particulate exposure, there was no significant correlation using either P or GMOE monitoring.

We conclude that assessment of personal exposure and season of the year as well as study design and methods of data analysis (cross-sectional vs longitudinal) are important factors in determining health effects of air pollution.

INTRODUCTION

Studies of health effects of air pollution, particularly at low levels, are often inconclusive due to limitations in assessments of both exposure and response. Until recently, estimates of exposure have relied upon measurements made at fixed outdoor sites usually oriented for source control purposes. It is now recognized that there are not only variations in pollutant levels horizontally and vertically but that the indoor environment can be vastly different from the outdoor environment. Thus, the actual exposures of an individual or the population may not be adequately represented by one or even more fixed outdoor sites. Studies using severe signs or symptoms of response largely ignore more minor fluctuations in health status, e.g. asthma. Definitions of subject populations with respect to differences in diagnostic criteria, health status, measures of sensitivity and objective measures, e.g. pulmonary function are either not clear, not uniform or absent. To address these issues a study was designed using well-defined subjects, objective (pulmonary function) as well as subjective (symptoms) measures of response, and personal air pollution measurements to assess the actual exposure of the subjects; air pollution data were also obtained from a central fixed outdoor site.

METHODS

Exposure to particulate matter and pulmonary function

(at the beginning and end of exposure monitoring) were examined in 2 groups of asthmatics as they went about their daily activities. The subjects carried personal samplers for a 6-8 hour period beginning between 8:00 and 9:00 A.M. and ending between 3:00 and 5:00 P.M. Each subject was monitored for approximately 20 days (10 days in the winter or heating season and 10 days in the summer or non-heating season). On each day, pulmonary function (spirometry) was obtained in the morning when the sampler was switched on and at the end of sampling. Using personal samplers, one group (Study 1) was monitored for exposure to particulate matter $< 25 \mu\text{m}$ in diameter (PS_1) and the other group (Study 2) to $< 10 \mu\text{m}$ diameter particles or respirable suspended particulate (PS_2). There were 17 asthmatics in Study 1 and 19 asthmatics in Study 2.

Subject selection. Subjects were selected from a pool of approximately 800 asthmatics in the patient population of an Asthma Clinic at The Gage Research Institute, a tertiary referral centre in Toronto for patients with lung disease. The patient population is weighted with patients with more severe asthma who tend to have a higher frequency of symptoms and might be expected to be more compromised by inhaling irritant pollutants than asthmatics having infrequent symptoms. The certainty of the diagnosis of asthma in patients attending the Asthma Clinic is established using uniform criteria based on history (consistent with

intermittent diffuse airways obstruction), physical examination (diffuse expiratory rhonchi), pulmonary function tests and reversibility of airways obstruction (after inhalation of the bronchodilator salbutamol). Patients were selected based on 1) a diagnosis of asthma and 2) wheezing at least a few times a week as recorded on their most recent visit to the clinic and verified by a preliminary questionnaire. Primary patient care was carried out by the patients' physician. Medications were not controlled for in the study but were used as a possible response variable.

Exposure assessment. Subjects carried a portable personal multipollutant sampler for SO_2 , NO_2 and one of 2 size fractions of particulate matter. Only the results of the particulate sampling will be presented in this report. Air pollution sampling was carried out from Monday to Friday for a total of 4 weeks for each participant; 2 weeks in the heating season and 2 weeks in the non-heating season. The personal sampler was worn either on a shoulder strap or a belt around the waist.

The sampler used for these studies was designed and developed at The Gage Research Institute (1) and is small, portable, low weight and low noise. It is a battery operated pump system, consisting of a filter assembly leading to 2 impingers, each containing the appropriate absorbing reagent. The samplers were prepared and checked in the laboratory each day before they were taken into the field for use. At the

start of the sampling period, the air flow was recorded and the timer started. The subjects were instructed on the proper care and use of the personal samplers. At the end of the sampling period, the flows and elapsed times of each sampler were recorded. The filters were stored flat in small covered Petri dishes until conditioning and weighing could be completed. Calibration and quality control procedures have been reported previously (1-3). As part of our on-going quality control program, a Gage sampler was also operated simultaneously at a central Ministry of the Environment (MOE) air pollution monitoring network station in downtown Toronto (26 Broadalbane). The sampler was placed inside an insulated, temperature regulated container (Koolatron) with the filter and NO_2/SO_2 inlets protruding from the Koolatron unit. This also provided us with the data to compare personal sampling with fixed-site sampling using the same techniques in both cases.

Two different particle size fractions were collected in the two studies. In Study 1, particulate matter was collected on a filter cassette (37 mm diameter open face) with a 1.0 μm fluoropore filter. The inlet dimensions and flow rates (0.9 L/min) were selected so that entrainment of particles up to approximately 25 μm size occurs. In the second study (Study 2), particulate sampling was carried out by drawing air through the filter placed in the filter cassette holder and mounted on a nylon cyclone (10 mm inside

diameter, 10 cm length). Particles less than 10 μm were collected on the filter, at a flow rate of 1.7 L/min. Under these conditions, the cyclone is reported to have a 50% particle cut point (aerodynamic particle diameter) of 5 μm (4).

Activities and health effects assessment.

Diaries. The subjects recorded daily information with respect to their clinical status in a diary form. Diary information included an asthma symptom day score and night score both rated on a scale from 0 (no wheeze) to 5 (continuous wheezing or awake all night wheezing), as well as medication use per 24-hour period. Further information included documentation of the time over which the personal samplers were worn, where and for how long the subjects were in any given location, and exposure to other potential inhaled irritants.

Pulmonary function. Tests of lung function were performed on the subjects at the beginning and end of each monitoring period using a wedge-balloon spirometer (Vitalograph). Measurements made included: forced vital capacity (FVC), forced expiratory volume in one second (FEV_1) and forced expiratory flow during the middle half of a maximum expiratory manoeuvre ($\text{FEF}_{25\%-75\%\text{VC}}$) and the ratio of FEV_1/FVC . The tests were administered according to standard recommended procedures (5). At each test session, at least 3 maximum expiratory manoeuvres were performed by the subjects

until 2 spiograms were obtained which were reproducible to within 5% for FVC. The Vitalograph was calibrated monthly for both volume (using a 1-litre syringe), and time.

Data analysis. All data were coded, keypunched and verified. Data management and statistical analyses were carried out using the University of Toronto computer and statistical packages SAS and BMDP (6,7).

Data were included in the analysis if they met all of the following criteria: 1) on a given day, all of the mean pulmonary function (mean FVC, mean FEV₁, mean FEF_{25-75%}VC), personal particulate and Gage MOE particulate measurements were available on an individual, 2) each person contributed at least 2 sets of observations per season, 3) each subject had these measurements in both seasons.

The data were analyzed using a longitudinal analysis whereby a slope was calculated for each subject for the line of best fit relating the daily mean (of the morning and afternoon values) of each pulmonary function variable (FVC, FEV₁, FEF_{25-75%}VC, FEV₁/FVC) with the corresponding day's particulate exposure, over all the days of monitoring. Slopes were obtained separately for each of the pulmonary function variables and each of the 2 particulate fractions. For a given individual, if pollutant exposure (increase) were to affect pulmonary function adversely (decrease), the relationship between daily mean pulmonary function and daily particulate exposure would be expected to have a negative

slope.

The data was also subjected to a cross sectional analysis by correlating pulmonary function and particulate exposure. For each individual, an average pulmonary function was calculated using the daily mean pulmonary function (of the morning and afternoon values) over all the days a given individual was monitored, and over the same days, an average of the daily particulate exposures of the individual was calculated.

RESULTS

The subjects in the 2 groups (Study 1 and Study 2) were similar with respect to age, height and weight with a ratio of females to males of approximately 3 to 1 (Table 1). Table 2 shows that there were no significant differences in mean pulmonary function ($p > 0.05$) between the 2 groups or between summer and winter. In Study 1, the personal sampler (PS_1) and the Gage sampler located at the MOE downtown air pollution monitoring station (GMOE) recorded the same particulate values ($p > 0.05$) in the summer. However, in the winter, the GMOE sampler underestimated the personal exposure (PS_1) by approximately $25 \mu\text{g}/\text{m}^3$ ($p < 0.02$); the mean winter GMOE data were also approximately $25 \mu\text{g}/\text{m}^3$ lower than in the summer. In Study 2, the mean particulate values were, as expected due to the smaller particulate fraction size, lower than in Study 1, and the GMOE values were $12\text{--}15 \mu\text{g}/\text{m}^3$ lower than the personal exposure (PS_2) values ($p < 0.006$). When

the data were combined across seasons, the GMOE sampler underestimated personal exposure in both Study 1 and Study 2 ($p = 0.05$ and 0.0003 respectively) .

Table 3 shows the results of a 2-way analysis of variance for the slopes relating mean pulmonary function and exposure to particulates as assessed by the personal sampler. Individual and season were used as factors in the model. For Study 1, the seasonal effect approached statistical significance ($p = 0.09$) only for the daily mean $FEF_{25-75\%VC}$. There was, however, a significant seasonal effect ($p < 0.04$) in Study 2 for three of the four pulmonary function variables (FVC , FEV_1 and $FEF_{25-75\%VC}$) with the fourth variable (FEV_1/FVC) of borderline or marginal significance ($p < 0.07$). When the information was combined across the 2 studies using Fisher's Method of Combining information (8), two of the four pulmonary function variables (FEV_1 and $FEF_{25-75\%VC}$) produced a significant seasonal effect ($p < 0.02$). There was a tendency for the slopes to be negative in the summer and positive in winter. When the GMOE particulate exposure levels were used, no significant findings were observed, i.e. there were no significant relationships between daily mean pulmonary function and particulate levels measured at the fixed downtown site.

Using the correlation or cross-sectional analysis (Table 4), the only significant correlation ($p < 0.01$) was in Study 1, for the FEV_1/FVC ratio ($r = -0.58$) using the personal

monitoring data in summer; FEF_{25-75%}VC during the same season was of borderline significance ($p < 0.07$). None of the other pulmonary function variables were significantly correlated with either personal or GMOE particulate exposures.

DISCUSSION

The data suggest that there is a seasonal difference with respect to relationships between a person's pulmonary function and exposure to particulate matter. In summer, as might be expected, there is a tendency for pulmonary function to decrease as exposure increases, i.e. an adverse effect of particulates on the lung. In winter, however, the opposite appears to be the case, namely, pulmonary function increases with increasing exposure and this appeared stronger in Study 2 in which the smaller or respirable particulate fraction was measured as an assessment of exposure. One interpretation of this data, the more common way, is that increased exposure to particulates improves pulmonary function; an alternative explanation could be that when pulmonary function is better, on a given day, an asthmatic may be able to tolerate higher particulate levels. In other words, when pulmonary function is lower, an asthmatic may limit his/her exposure to atmospheres which contain less particulates. This would be consistent with the "healthy worker effect" described in occupational studies where there is a self-selection as individuals who are compromised by some exposure select themselves out of that work environment

or remove themselves from it (9-11).

However, another explanation is an interaction with some other confounding variable or variables, such as medication use, other environmental exposures or conditions, temperature, humidity, etc.

Another important observation confirms what we have found previously (12,13), that in terms of assessing health effects of air pollution, the particulate levels measured at a fixed-site remote from the subjects' whose health is being assessed may not be a suitable indicator of actual exposure. This was reinforced by the observation that the significant relationships between pulmonary function and personal exposure were not present when the exposure data from the downtown Toronto site were used. The resolution of data from fixed-site sampling might be improved by taking into account factors such as the activity pattern of the subjects, and using multiple sampling sites (both indoors and outdoors) to adjust the data to approximate personal exposure.

Finally, the significant findings appeared with the longitudinal (slopes) analysis whereas the cross-sectional (correlations) analysis would not have uncovered the significant relationships. Thus the method of data analysis, i.e. cross-sectional vs longitudinal, has an important impact on the final interpretation of the experimental results.

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TABLE 1. Anthropometric Data*

	Sex M/F+	Age** (yr)	Height** (cm)	Weight** (kg)
Study 1 (n=17)++	5/12	50.0 \pm 14.9	165.2 \pm 8.9	65.3 \pm 11.4
Study 2 (n=19)	4/15	48.2 \pm 14.2	167.8 \pm 8.4	64.7 \pm 11.4
Overall (n=30)+++	8/22	47.9 \pm 14.1	166.6 \pm 8.5	65.4 \pm 11.0

* Values are mean \pm standard deviation.

+ M=males, F=females.

** Age in years, height in centimeters, weight in kilograms.

++ n=number of subjects.

+++ There were 6 subjects who participated in both studies.

TABLE 2. Mean Pulmonary Function and Mean Particulate Exposures*

	<u>Study 1</u>		
	Summer (n=17)	Winter (n=17)	p** values
<u>Pulmonary function</u>			
FVC+ (l)	3.14 ± 0.99	3.12 ± 0.91	0.96
FEV ₁ (l)	2.18 ± 0.84	2.11 ± 0.74	0.87
FEF _{25-75%VC} (l/sec)	1.65 ± 1.11	1.49 ± 0.94	0.65
FEV ₁ /FVC	0.68 ± 0.11	0.68 ± 0.11	0.86
<u>Particulate</u>			
PS ₁ -personal (µg/m ³)	108.5 ± 31.0	108.9 ± 36.5	0.97
-GMOE (µg/m ³)	106.4 ± 29.0	84.3 ± 17.5	0.01

	<u>Study 2</u>		
	Summer (n=19)	Winter (n=19)	p values
<u>Pulmonary function</u>			
FVC (l)	3.37 ± 0.92	3.20 ± 0.98	0.58
FEV ₁ (l)	2.36 ± 0.81	2.21 ± 0.89	0.60
FEF _{25-75%VC} (l/sec)	1.71 ± 0.91	1.61 ± 0.92	0.73
FEV ₁ /FVC	0.69 ± 0.11	0.67 ± 0.12	0.67
<u>Particulate</u>			
PS ₂ -personal (µg/m ³)	49.6 ± 15.4	50.4 ± 14.2	0.87
-GMOE (µg/m ³)	37.9 ± 7.5	35.6 ± 5.5	0.30

* Mean ± standard deviation.

+ Definitions FVC=forced vital capacity in liters; FEV₁=forced expiratory volume in 1 second in liters; FEF_{25-75%}VC= forced expiratory flow during the middle half of a maximum expiratory manoeuvre in liters per second; FEV₁/FVC=ratio of FEV₁/FVC; PS₁=particulate concentration in Study 1; PS₂=particulate concentration in Study 2; Personal=personal sampler; GMOE=Gage sampler located at the fixed MOE downtown site.

** p values associated with the null hypothesis of no seasonal effect.

TABLE 3. Slopes of daily mean pulmonary function and daily personal particulate exposures

	STUDY 1 (n=17)		p* values	STUDY 2 (n=19)		p* values	OVERALL p** values
	summer slope+	winter slope	season	summer slope	winter slope	season	season
FVC++	-0.46	0.06	0.54	-0.65	2.58	0.04	0.10
FEV ₁	-0.78	0.18	0.26	-1.65	2.83	0.01	0.02
FEF _{25-75%} VC	-2.03	-0.10	0.09	-1.13	4.40	0.03	0.02
FEV ₁ /FVC	-0.13	0.12	0.22	-0.33	0.33	0.07	0.10

+ Mean slopes of the relationships between each subject's daily mean pulmonary function and daily mean personal particulate exposure multiplied by 1000.

++ Pulmonary function variable for which slope was calculated.

* p values associated with a 2-way analysis of variance of the slopes; factors are season and individual.

** Fisher's Method of Combining Information.

TABLE 4. Correlations of mean pulmonary function with mean personal and fixed-site particulate exposures

STUDY 1

(n = 17)

	SUMMER				WINTER			
	Personal++		GMOE++		Personal		GMOE	
	r+	p*	r	p	r	p	r	p
FVC	-0.15	0.58	0.32	0.21	-0.03	0.92	0.03	0.92
FEV ₁	-0.34	0.18	0.19	0.47	-0.16	0.53	0.03	0.90
FEF _{25-75%} VC	-0.45	0.07	0.02	0.95	-0.29	0.26	-0.04	0.88
FEV ₁ /FVC	-0.58	0.01	-0.06	0.81	-0.37	0.14	0.05	0.84

STUDY 2

(n = 19)

FVC	-0.06	0.80	0.30	0.21	-0.05	0.84	-0.12	0.64
FEV ₁	-0.07	0.78	0.32	0.19	-0.10	0.68	-0.18	0.46
FEF _{25-75%} VC	-0.01	0.98	0.35	0.14	-0.14	0.56	-0.19	0.43
FEV ₁ /FVC	-0.07	0.75	0.14	0.58	-0.17	0.48	-0.21	0.39

+ Pearson's Product-Moment Correlation Coefficient between overall mean pulmonary function and overall mean particulate exposure for each individual.

* p values associated with the null hypothesis of no significant correlation (i.e. $r=0$).

++ Personal = personal sampler; GMOE = Gage sampler located at the fixed MOE downtown site.

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ASSESSMENT OF TOXICITY OF DIGESTED AND INHALED
HALOAROMATIC HYDROCARBONS

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Introduction

Appreciation of potential toxicity of environmental pollutants for humans is facilitated by studies in animal species. Although there may be considerable difference in the dose of an agent required to produce significant toxicity, animal models provide insight as to what sorts of effects could be tested for in humans. This becomes particularly important where human exposure is chronic, low level, and where the exposure produces biological effects without causing overt acute illness.

We have been particularly interested in the effects of chronic exposure to halogenated aromatic hydrocarbons such as dibenzodioxins, PCBs, dibenzofurans, and related haloaromatics. In most industrialized countries, the population is exposed to some degree through food, water, air, and in the case of infants, breast milk (1). Accidental high-level exposure to such agents can cause overt illness in both humans and domestic animals (2,3). The effects of low dose exposure are unknown, but do lead to fear and sensationalism, if not disease in the long term (4). To better understand the effects on mammals of chronic low-dose exposure to haloaromatics, we have focused on the immune system. In all animals species studied to date, exposure to agents such as 2,3,7,8-TCDD, one of the most potent of the haloaromatics, consistently produces damage to the thymus gland (5). The thymus is an organ that generates T(thymus-derived) lymphocytes required for a functioning immune system. T cells may act as effectors of cellular immunity (killer T cells and T cells producing delayed hypersensitivity), or they may act as regulatory T helper and T suppressor cells. T helper cells are required for most types of immunity, both cellular immunity and formation of antibodies, and their destruction (as typified by AIDS) with unopposed T suppressor cell activity, can be fatal (6). In the case of viral infection, stimulation of suppressor cells may even be a factor necessary for a virus to establish itself after exposure.

Figure 1 illustrates the system we have developed to test the effect of exposure of laboratory mice to haloararomatics on immune function. Our initial studies were done by injecting high doses of TCDD or related haloaromatics and measuring the immune response to antigen challenge. As expected, high doses of TCDD produced thymus gland atrophy, illness (with weight loss), and suppressed both T cell and antibody responses. At lower doses, the animals appeared healthy and the thymus gland grossly normal, but the immune response still impaired. We found, however, that only the killer T cell response was affected. (7).

In vitro analysis

To determine how TCDD was affecting the killer T cell (CTL or cytotoxic cell) response, we used the system reviewed in Figure 2.

Figure 1

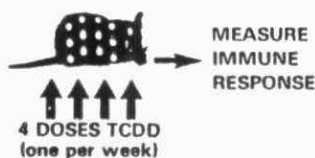
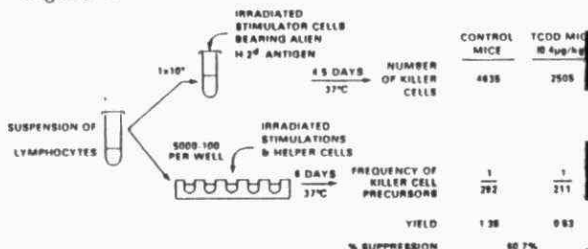


Figure 2



This methodology allowed us to determine how many CTL were generated from each precursor and to evaluate changes in T helper and T suppressor activity. With this approach we reached the following conclusions:

- (1) 2,3,7,8-TCDD impairs the CTL response by stimulating suppressor T cell activity (8). This comes about by an effect of TCDD on the epithelial cells of the thymus that control T development (8-10). T suppressor cells of the short-lived subset are then overproduced (8-10).
- (2) Suppression by 2,3,7,8-TCDD occurs at a cumulative dose of 12 pM (10^{-11} M or 4 ng/kg).
- (3) Similar suppression is produced by PCBs such as 3,4,3',4'-TCB and Aroclor 1254 (11).

Validity of suppression measured in vitro

Evidence that suppression by very low doses of TCDD represented a real biologic effect was shown by:

- (1) Genetics. Sensitivity to TCDD is determined by genes at the Ah locus in mice (7). It is believed that genetic determination of susceptibility or relative resistance is determined by the Ah locus-controlled level of a cytoplasmic receptor protein, to which TCDD binds, although there has been some controversy about the significance of the level of receptor in susceptibility (12,13). Use of genetically sensitive and resistant mice allowed us to demonstrate the importance of thymic epithelium (that possesses Ah-regulated TCDD-receptor) in determining responsiveness to TCDD.

- 2) Thymectomy. Removal of the thymus prevented suppression, and a similar loss of susceptibility was found when mice were aged to allow natural thymic atrophy to occur (9). We also showed that following challenge with herpes virus type 2 mortality was increased in TCDD-treated mice (11). Resistance to this virus is mediated in part by CTL. We did not show, however, that the CTL response in infected animals was impaired, and we only tested the effect of TCDD doses down to 120 pM (40 ng/kg). We therefore did some experiments at the 12 pM dose to determine if CTL responses were impaired in the intact mouse.

Table 1 shows that CTL responses were indeed suppressed whereas significant suppression of antibody responses and DTH responses could not be detected (unpublished data). Therefore, the suppression measured in vitro appears to reflect immune impairment in vivo.

Table 1

Effect of 12 pM cumulative dose of 2,3,7,8-TCDD on immune responses of C57Bl/6 male mice in vivo.

Types of Responses	Group	Antigen	Response
Cytotoxic T cell	Controls	Irradiated PB15	CTL Yield/mouse \pm SEM
	TCDD	" "	55.2 \pm 4.6 32.1 \pm 2.6
			$P \leq 0.05$
DTH	Controls	Topical DNFB	Ear swelling units(7)
	TCDD	" "	15.4 \pm 3.1 15.1 \pm 5.3
			$P = N.S.$
Antibody	Controls	SRBC ip	Serum titre (log 2)
	TCDD	" "	4.27 \pm 1.02 4.24 \pm 1.38
			$P = N.S.$

Comparisons of isomers of haloaromatics

There are a variety of haloaromatics in the environment and human exposure usually involves mixtures of different compounds (1). The first step in understanding the possible effects of mixtures is to examine the individual components. One can then test combinations and create a mixture the composition of which is defined. Finally, one can test what occurs in the environment, such as fly ash that is generated by incinerators (1). It is always possible that naturally occurring pollutants will not behave as predicted due to the presence of small amounts of compounds the importance of which has not yet been recognized.

Although one could argue that proceeding to a direct test of the naturally occurring pollutant is more expeditious, the more analytical approach outlined above is more efficient in the long run, is less likely to produce confusion and unanswered questions, and is more likely to be practically applicable. Mixtures in nature can vary considerably in composition and may therefore give variable results that cannot be explained. (14)

Figures 3-7 show the HPLC and mass spectra for purified isomers of dibenzodioxins and dibenzofurans provided by Wellington Laboratories, Guelph, Ontario. We performed dose-response studies of each compound as well as repeating our 2,3,7,8-TCDD positive control, and obtained the result shown in Figure 8. It can be seen that the 2,3,7,8 tetrachloro-dibenzofuran was also highly suppressive whereas addition of a Cl at the 4, and 4 + 6 positions markedly reduced potency. Similarly, addition of Cl to the 1 and 1+4 positions of TCDD reduced potency.

Effect of exposure of non-parenteral route

All of the studies described above were done by injecting the test compound into the animals. This ensured that they had received a known amount of haloaromatic. Natural exposure in the environment occurs by quite a different route, however. In the case of food and water contaminants, the GI tract is involved. With smokes containing haloaromatics such as TCDD, most particles settle in lung bronchi. While it is possible that some absorption into the body occurs at that site, haloaromatics being hydrophobic and insoluble in water are likely to remain in the smoke particles in the mucus layer and when this mucus is wafted centrally and up into the throat area and swallowed (as normally occurs), the GI tract will be exposed (15). The GI tract is quite able to absorb lipids and lipophilic compounds. We therefore decided to test the effect of oral feeding of TCDD and related haloaromatics for effects on CTL generation in vitro.

Table 2

Effect of oral feeding of 2,3,7,8-TCDD on CTL generation in vitro

Expt	Dose Range Used	Suppression In: Lymph Nodes	Spleen	Comment
1.	4 ug/kg	+	++	ERR in liver
2.	0.004-0.04 ug/kg	0	++	----
3.	0.4-4 ug/kg	0	+	----
4.	0.004-4 ug/kg	0	0	Same lot of mice suppressed with TCDD injected ip
5.	0.004-40 ug/kg	++	0	ERR in liver (see figure 10)
0 = no suppression				

Table 2 summarizes the results from a number of studies we have done with oral feeding of 2,3,7,8-TCDD. It can be seen that suppression could be produced but that results were variable between experiments. This variability did not appear to be explainable by failure of the animals to eat the TCDD-impregnated feed. Part of the variation appears to be explainable by the fact that circulating suppressor cells released from the thymus may not settle in the lymph nodes or spleen unless these organs are stimulated prior to their removal for testing in vitro. With injection into the the peritoneal cavity, the trauma itself creates a degree of stimulation. In fed mice, the degree of activation of spleen and lymph nodes is also determined by the bacterial flora in the gut, and this can vary considerable from season to season, from year to year, and among shipments of animals from the supplier.

The possibility that absorption of TCDD might be affected is being tested by measuring ERR activation in liver at the higher dose levels. ERR stimulation without immunosuppression would be consistent with our hypothesis but in two studies of ERR activation done to date immunosuppressor occurred as expected when the oral route was used. Since an immune response in vivo also activates lymph nodes or spleen, accumulation of suppressor type cells from the circulation would be expected and therefore, it is possible that in vivo testing as shown in Table 1 could be more reliable in evaluating the effects on orally fed haloaromatics.

Figures 9 shows the effects of the injected haloaromatic isomers on liver weight as a % of body weight. The effect of oral TCDD is also shown. Figure 10 shows the effect of the isomers (shown in Figures 3-7) on hepatic ERR activity. The effect of oral feeding of TCDD is also shown. Assays are currently being done to test the effect on CTL generation of the orally fed isomers and this data will be presented on November 30, 1987 at the Technology Transfer Conference.

Summary and conclusions

Immunosuppression by 2,3,7,8,-TCDD is a real biologic effect that occurs at extraordinarily low doses. Suppression occurs under chronic exposure conditions and has not been detected with acute exposure studies (9). Suppression by low dose exposure selectively impairs the CTL response and may be localized to only certain sites depending upon activation of the lymphoid organ being tested.

A great deal of work still must be done to fully understand the effects of haloaromatics on host immunity and to apply these findings. Mixtures of the compounds already tested individually in figures as well as naturally occurring mixtures need to be studied. Factors affecting absorption of orally injected smoke particles need to be assessed, and in vivo immune responses must be compared to in vitro assays of killer T cell responses. Practical and safe methods need to be developed to evaluate the effect of haloaromatic-contaminated smokes where particle size (and hence pattern of deposition and absorptive site) can be controlled.

The potential importance of controlled studies using experimental animals derives from the fact that one can define "zero" effect doses and evaluate mixtures to which humans are exposed. There is increasing evidence there may be subclinical immunosuppression in those who are young and still have a functioning thymus gland when exposed (16-18), and regulations with respect to permissible exposure levels currently have to be made with incomplete knowledge of the possible and probable effects of the various haloaromatics in the environment.

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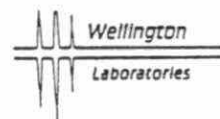
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CHEMICAL STANDARD - DOCUMENTATION SHEET



COMPOUND: 12378-Pentachlorodibenzo-p-dioxin

LOT NUMBER: 12378-DD-01

☒CRYSTAL

☐SOLUTION

SOLVENT:

CONCENTRATION:

PURITY: > 98%

LAST PURIFICATION STEP: Column Chromatography

GC/MS DATA:

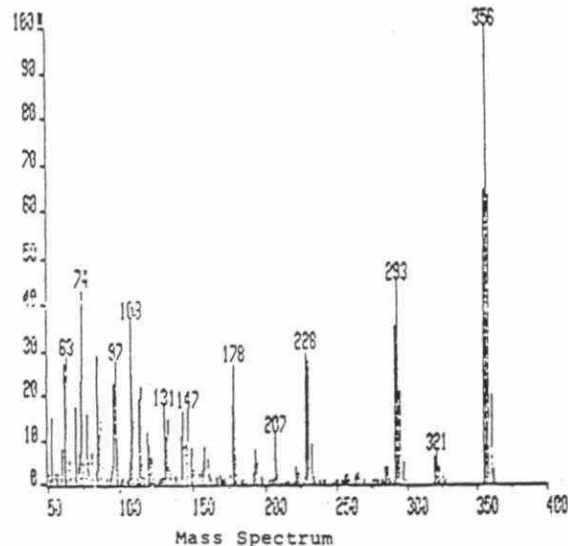
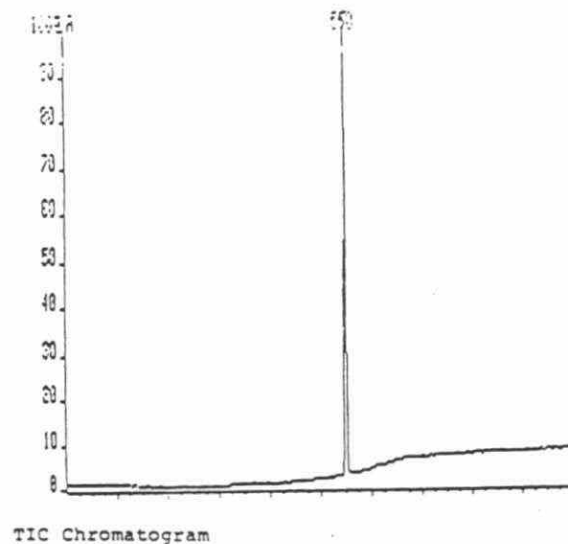


Figure 3

CHEMICAL STANDARD - DOCUMENTATION SHEET



COMPOUND: 123478-Hexachlorodibenzo-p-dioxin

LOT NUMBER: 123478-DD-01

☒CRYSTAL

☐SOLUTION

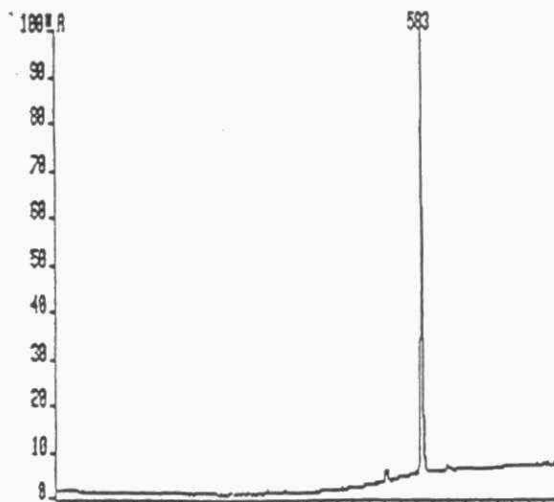
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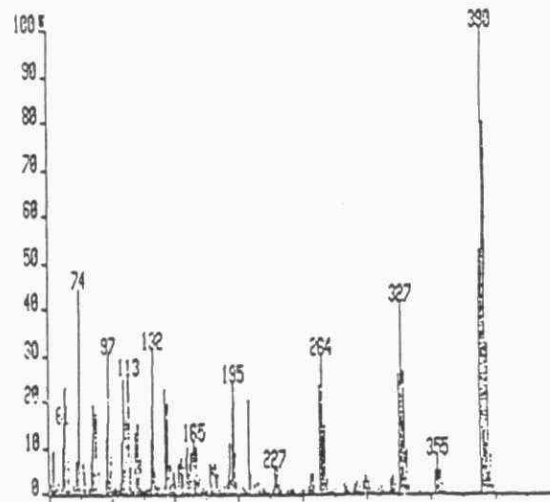
PURITY: >95%
(Cl₅ DD impurity)

LAST PURIFICATION STEP: TLC

GC/MS DATA:



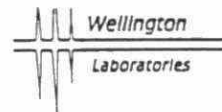
TIC Chromatogram



Mass Spectrum

Figure 4

CHEMICAL STANDARD - DOCUMENTATION SHEET



COMPOUND: 234678-Hexachlorodibenzofuran

LOT NUMBER: 234678-DF-01

☒CRYSTAL

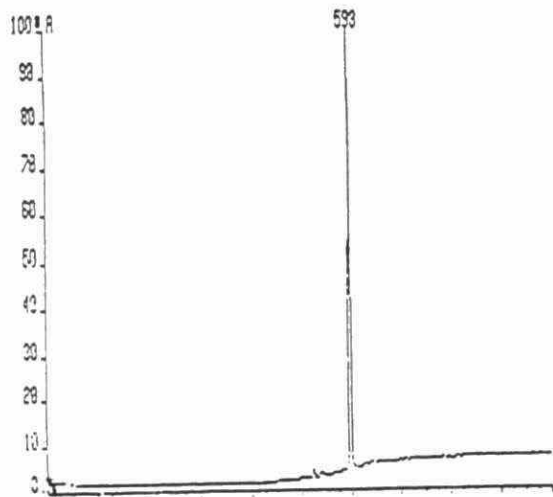
☐SOLUTION

SOLVENT:
CONCENTRATION:

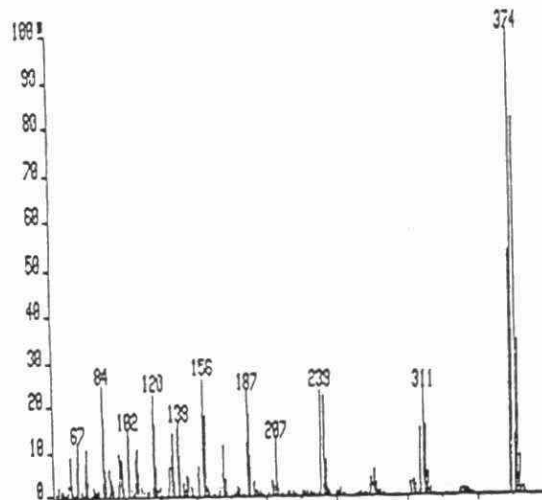
PURITY: >98%

LAST PURIFICATION STEP: TLC

GC/MS DATA:



TIC Chromatogram



Mass Spectrum

Figure 5

CHEMICAL STANDARD - DOCUMENTATION SHEET



COMPOUND: 2378-Tetrachlorodibenzofuran

LOT NUMBER: 2378-DF-01

☒ CRYSTAL

☐ SOLUTION

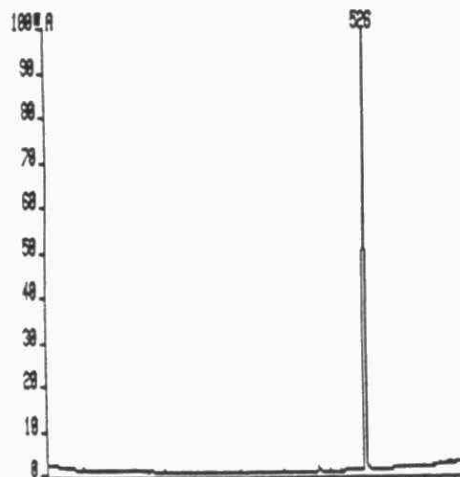
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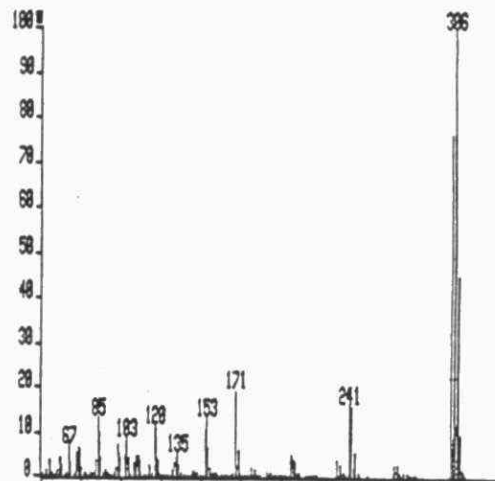
PURITY: > 98%

LAST PURIFICATION STEP: Recrystallization

GC/MS DATA:



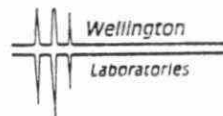
TIC Chromatogram



Mass Spectrum

Figure 6

CHEMICAL STANDARD - DOCUMENTATION SHEET



COMPOUND: 23478-Pentachlorodibenzofuran

LOT NUMBER: 23478-DF-01

☒CRYSTAL

☐SOLUTION

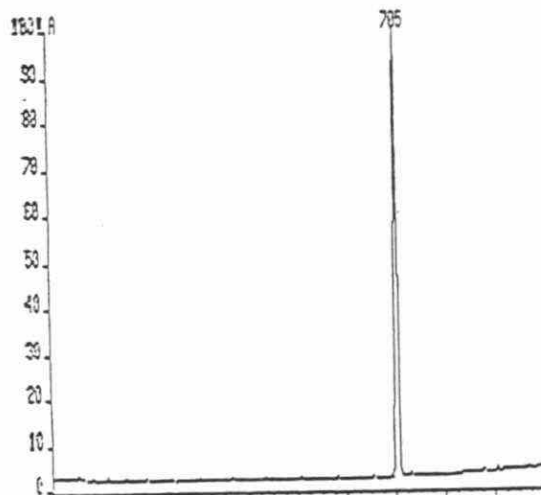
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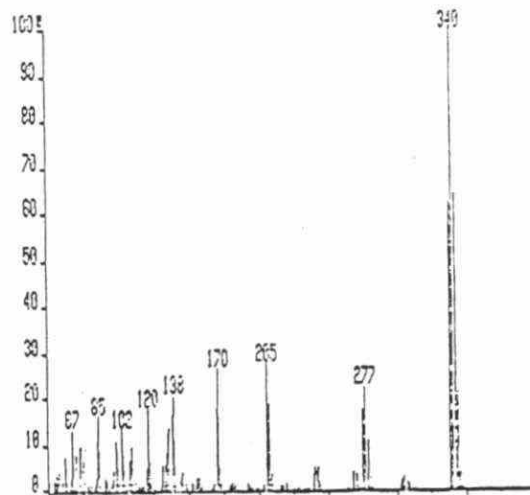
PURITY: >98%

LAST PURIFICATION STEP: TLC

GC/MS DATA:



TIC Chromatogram



Mass Spectrum

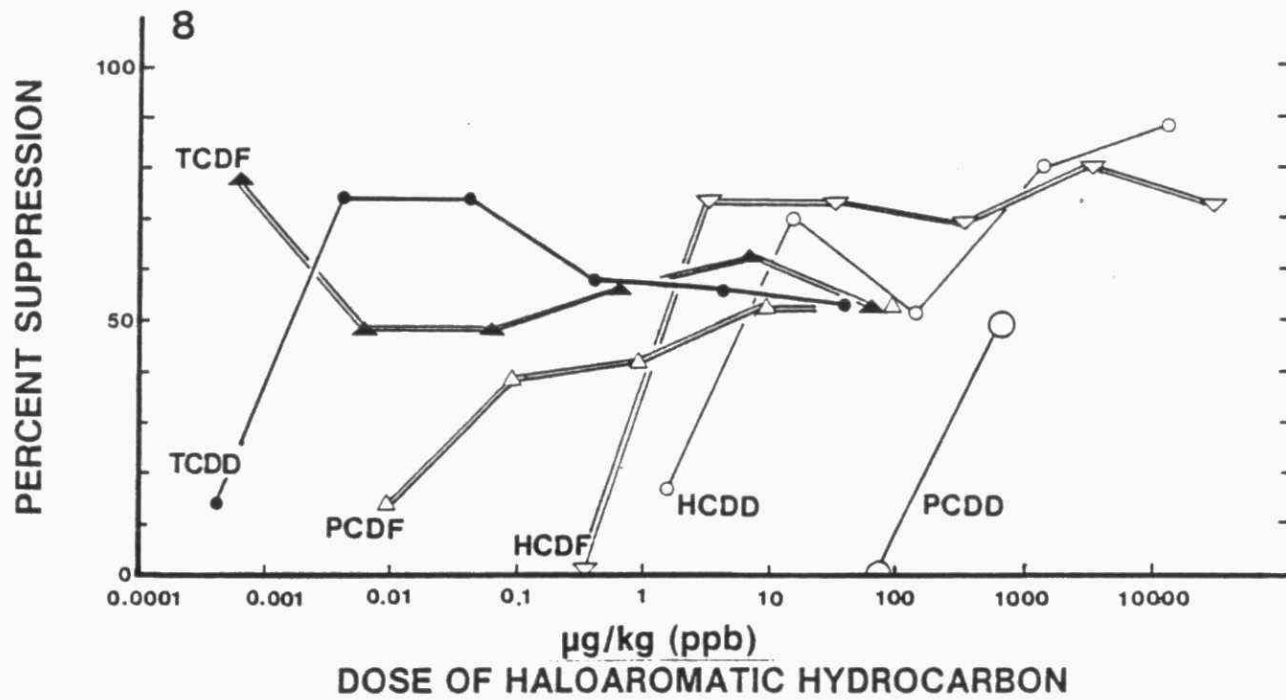
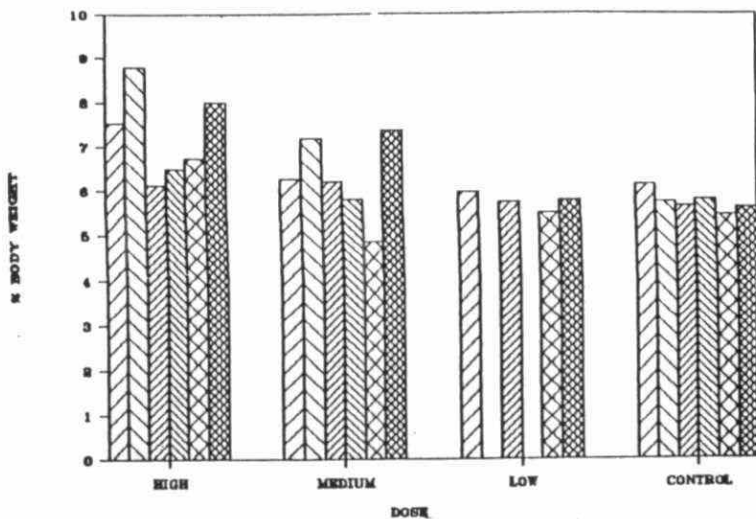


Figure 8

Figure 9

Liver Weight as % of Body Weight



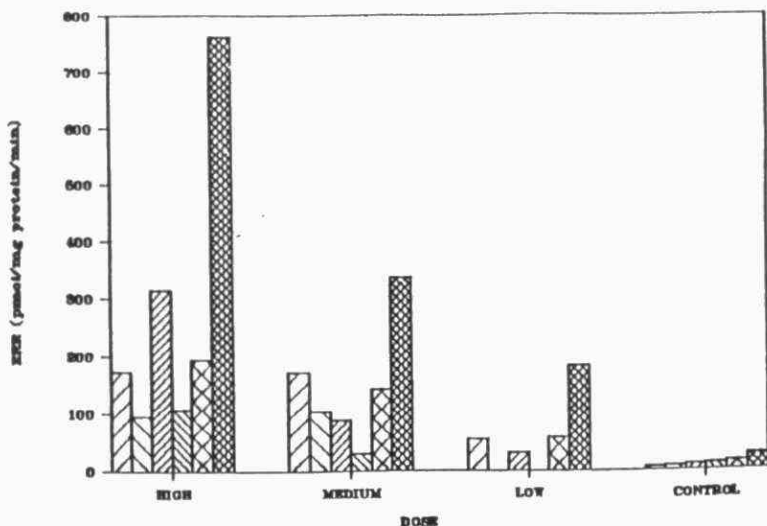
COMPOUND TESTED	ROUTE	DOSE ($\mu\text{g/kg/wk} \times 4$)		
		HIGH	MEDIUM	LOW
1,2,3,7,8-PCDD	inject	72	7.2	0.72
1,2,3,4,7,8-TCDD	"	1440	144	--
2,3,4,6,7,8-TCDF	"	320	32	3.2
2,3,7,8-TCDF	"	60	6.0	--
2,3,4,7,8-PCDF	"	90	9.0	0.9
2,3,7,8-TCDD	oral	46.8	3.16	0.436

xxDF = dibenzofuran

xxDD = dibenzodioxin

ERR ACTIVITY

Figure 10



COMPOUND TESTED	ROUTE	DOSE (µg/kg/wk x 4)		
		HIGH	MEDIUM	LOW
1,2,3,7,8-PCDD	inject	72	7.2	0.72
1,2,3,4,7,8-HCDD	"	1440	144	--
2,3,4,6,7,8-HCDF	"	320	32	3.2
2,3,7,8-TCDF	"	60	6.0	--
2,3,4,7,8-PCDF	"	90	9.0	0.9
2,3,7,8-TCDD	oral	46.8	3.16	0.436

xxDF = dibenzofuran

xxDD = dibenzodioxin

SUMMARY

One of the health hazards arising from the inhalation of polluted air is cancer of the lung and trachea. Establishment of appropriate limits for airborne pollutants so as to eliminate or minimize this hazard is an important goal. Unfortunately, both epidemiological studies and animal cancer bioassays are too cumbersome to be very useful guides for the creation of detailed regulatory standards. This project is dedicated to the development of in vivo measurements of the somatic mutation rate in the relevant tissue as a more relevant biological standard than any now available. The central role played by mutation in the carcinogenic process suggests that mutation rates are a relevant biological endpoint for such standards.

Mutation rates in mammalian cells are normally measured by determining the fraction of cells that can form colonies under selective conditions, such as toxic concentrations of a drug: those cells have mutated to resistance to the drug will grow to form colonies even in its presence, whereas nonmutants will not grow and will not form colonies. The mutation rate can thus be computed from the fraction of cells that can form colonies in the presence of the drug. But such an assay cannot be conducted on cells unless they form colonies - and neither lung nor tracheal epithelial cells do. Hence we proposed to develop a novel assay for mutation that did not depend on colony formation. The concept was that mutant cells resistant to diphtheria toxin, a substance that kills sensitive cells by shutting down protein synthesis, would incorporate tritiated leucine into protein after exposure to the toxin, whereas sensitive cells would not. The assay had been shown to be successful in a cultured line of Chinese hamster cells.

In the first year our research aims were met on schedule and the techniques for isolating and culturing the cells were established (Report #1; Paper 1, Appendix A). The aims of the second year were to determine the conditions appropriate for measurement; the results of the year's work are the subject of this report and are being incorporated into three papers now in draft form (Appendices B, C, and D). The aims of the third year, for which funding is hereby requested, are to validate the assay by testing of known carcinogens under realistic conditions, as originally proposed.

During the second year the research did not proceed as planned. Although the techniques developed in the first year worked reproducibly, we were unable to discover satisfactory conditions for measurement of mutations by the proposed method (Paper 2, Appendix B). Hence we have found it necessary to develop an alternate approach, the use of fibroblasts. This approach has several advantages over our previous approach and, moreover, is working well (Papers 3 & 4, Appendices C & D). It is this technique that is ready to be validated in the third year of the grant.

In the lung the fibroblasts are closely apposed to the epithelial cells. Our initial work has shown that the fibroblasts are readily isolated and cloned, and that the lung specific carcinogen, urethane, can be detected using them. (It is noteworthy that urethane is not detected in the Ames Salmonella/mammalian microsome assay nor in other in vitro assays.) Two significant advantages accrue from using fibroblasts: (1) traditional methods for detecting mutations can be used (Dean and Senner, 1976; Manuscript 3, Appendix C), and (2) chromosomal aberrations can also be detected with the rapid micronucleus technique (Manuscript 4, Appendix D). This broadens the range of genetic events that can be detected and thus the range of carcinogenic exposures. Indeed, the response to urethane is very dramatic in the micronucleus data but is only marginally positive in the mutation assay.

FIVE YEAR STUDY USING A MOBILE RAIN EXCLUSION CANOPY SYSTEM TO DETERMINE JOINT EFFECTS OF SIMULATED ACID RAIN AND OZONE ON THE GROWTH AND PHYSIOLOGY OF SUGAR MAPLE AND WHITE SPRUCE SEEDLINGS

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Phytotoxicology Controlled Environment Laboratory,
100 Farmhouse Crt., Brampton, Ontario, L6V 9Z0

ABSTRACT

A fully automated rain exclusion canopy (REC) system, was designed and constructed at the Ontario Ministry of the Environment, Phytotoxicology laboratory in Brampton, Ontario for performing 'effects' studies with simulated acid rain (SAR). The REC system consists of three, mobile greenhouse shelters which exclude ambient rainfall and apply simulated acid rain treatments to tree seedlings established in field plots. The REC system was used in this, the initial year of a five year study, to determine the impact of controlled applications of simulated acid rain, alone and in combination with ozone, on the growth and physiology of potted sugar maple (*Acer saccharum*) seedlings and white spruce (*Picea glauca*) seedlings established in field plots. Seedling response is being monitored in the following ways: a) visible injury index, b) plant physical dimensions, c) leaf chlorophyll, d) stomatal conductance and rate of photosynthesis, e) elemental concentrations in foliar tissue. Soil solutions from selected tree replicates are also being collected and analyzed.

Prior to the field study, a preliminary experiment was conducted in the spring of 1987. Potted seedlings were grown in two soil types in the greenhouse and were placed in chambers for exposure to simulated acid rain and ozone. Trends observed in the preliminary greenhouse experiment suggest that ozone and soil type are both factors which may affect sugar maple seedling response to SAR; e.g. plant height, foliar chlorophyll, stomatal conductance. However, measurements made on seedlings in the REC plots during the initial summer of the REC field study have so far shown no significant treatment effects.

INTRODUCTION

At present, ambient levels of ozone occur in Ontario which may be injurious to crops and forest trees (Linzon et al., 1984). Evidence is increasing that forest declines such as maple dieback in Ontario and Quebec, may be related to acidic precipitation (McLaughlin et al. 1985). Furthermore, the joint effects of ozone combined with acidic rain containing both sulphate and nitrate ions have been suggested as important contributors to forest decline in recent years (Lefohn and Brocksen, 1984). The occurrence of episodes of elevated ambient ozone concentrations followed by acidic precipitation is currently a strongly supported hypothesis to explain forest damage in Europe (Linzon, 1985). Joint effects of acidic precipitation and ozone could be responsible for deleterious effects observed in sugar maple in Ontario.

Ozone and acid fog are being linked to recent dieback observed in red spruce in the northeastern U.S.A. (Jagels, 1986). Although Ontario is at the northern limit of the range of red spruce, white spruce, which grows throughout the province, has been shown to be as sensitive to SAR as red spruce (Percy, 1984). White spruce may be affected by increased rain acidity in Ontario. Work by Hutchison (1985), suggests that white spruce is sensitive to Al which has increased availability in acidified soils.

Therefore, a multi-year study has been initiated at the M.O.E. Phytotoxicology laboratory in Brampton to determine whether or not the interaction of ozone and SAR can induce either subtle physiological response and/or visible effects in sugar maple seedlings. White spruce seedlings were included in the study in order to investigate joint effects of SAR and O_3 on this conifer which, like sugar maple, is an important forest species in Ontario.

The joint effects of SAR and O_3 on tree seedlings are being investigated with a mobile rain exclusion canopy (REC) system which was designed and constructed by the Ontario Ministry of the Environment. REC systems of various designs have been utilized for simulated acid rain 'effects' studies with crops (Evans et al., 1981; Heagle et al., 1983; Irving, 1983). These field apparatus eliminate ambient acidic ion inputs which may interfere with controlled applications of simulated acid rain on test plants in the field.

The Ministry of the Environment REC system is unique because all aspects of canopy movement, treatment application and preparation are computer controlled. Also, a gaseous pollutant reduction system was included in the design. Filtered air is blown over test plants through perforated polyethylene tubes which run parallel to experimental plots. This design minimizes micro-climate effects which occur in open-topped chamber designs (Thompson and Olszyk, 1985).

MATERIALS AND METHODS

1. Field study with the rain exclusion canopy (REC) system

1.1 Description of the System

Test plants are grown on three separate treatment areas (15.2m x 7.6m) which are situated side by side in a west to east direction. During ambient rain events, these treatment areas are covered by three free-standing greenhouse structures (dimensions: 19.5m x 9.1m x 4.6m) constructed of galvanized steel and covered in polyethylene. At all other times, the shelters are stored in a position sufficiently south of the plots so as not to interfere with incident radiation to the treatment areas. Each treatment area is subdivided into 50 experimental plots (1.5m x 1.5m). Nozzles in each canopy are arranged in two 5x5 latin squares which allows for the simultaneous application of up to five SAR treatments (refer to Figure 1).

The stainless steel, whirl-jet nozzles (Bete Fog Nozzles Inc. Greenfield, Mass.) are mounted to the canopy frames 2.4m above the soil. Each nozzle is centred over its respective experimental plot when the canopy is positioned over the treatment area. Each nozzle emits a square pattern of droplets with a mean drop size of 1mm diameter. The whirl-jet design

provides total coverage of each plot. All components that are contact with SAR such as pumps, solenoid valves and regulators, tanks and treatment lines are constructed of non-corrosive materials (stainless steel, PVC, or black polyethylene).

Every aspect of the field system is controlled by a micro-computer (Apple IIE) and data acquisition device (Cyborg Isaac 91A). All control devices, treatment mixing tanks, treatment storage reservoirs, pumps and monitors are housed in a climate controlled trailer. Air quality (O_3 , SO_2 , NO/NO_2) are measured by monitors (Monitor Labs Inc. Model 8810 photometric O_3 analyzer, Teco Inc. Model 43 pulsed fluorescent SO_2 analyzer and Model 14B/E Chemiluminescent $NO_2/NO/NO_x$ analyzer). Temperature, relative humidity, wind velocity and photosynthetic photon flux density are measured by sensors located on an 8m tower attached to the control trailer. Ambient precipitation is detected with an electronic rain sensor and is measured with a tipping bucket rain gauge (Weathertronics Model 6010) situated on the trailer roof. Every 30 minutes, previous half hour means of all meteorological, air quality, and precipitation data are stored on floppy disk and the printed for permanent record.

When precipitation occurs, the computer immediately moves the canopies over the treatment areas. SAR is applied automatically on a time basis until the amount applied equals the ambient rainfall deposition as monitored by a tipping bucket rain gauge. SAR treatments are prepared automatically as required. The computer can also be programmed to apply a desired amount of SAR at a specified time. In the manual mode, SAR is applied in 0.8 mm increments within 10 minute intervals (4.8 mm hr^{-1}) until the predetermined amount is applied. Normal program routines such as air quality monitoring and meteorological data collection continue during SAR applications.

The air exclusion system consists of nine large blowers, potassium permanganate-treated alumina filters and polyethylene tubes. Air is blown into each treatment area via six 30cm diameter perforated polyethylene tubes or 'pillows' which run parallel to plot rows. Each pillow has six sets of holes arranged along its entire length. Holes vary in size from 1.0 mm to 1.3 mm diameter and are spaced 15cm apart. The computer controller activates blowers and the ozone generator if the half hour mean value of ambient ozone exceeds a 0.05 ppm criterion. Blowlers are deactivated when precipitation occurs or the half hour mean falls below the specified criterion level.

When activated, the air exclusion system blows filtered air into the treatment area of the west canopy to reduce elevated, ambient levels of gaseous pollutants (e.g. O_3 , SO_2 , NO_x). Plots of the east canopy are exposed to elevated ozone levels produced by an ozone generator (Griffin Model GTC -1B) and injected into the blower-pillow system to increase ambient ozone concentrations. Unfiltered ambient air is blown into plots of the centre canopy for control purposes.

A more detailed description of the various components and routines of the Ontario Ministry of the Environment mobile rain exclusion canopy system is given in another paper (Kuja *et al.*, 1986).

1.2 Soil Requirements for the Study

One objective of the study is to investigate tree seedlings grown in nutrient poor, acidic soil, typical of shield areas of the province. Soil nutritional status may be a potential factor in observed forest declines. During October, 1985, a total of 120 m³ of brunisol soil was removed from a site near Dorset (Lot 1, Concession A of Ridout Twp.) located on the side of Margret Lake Rd., 1 km south of the MNR Leslie Frost Centre. The organic A horizon was first removed from the soil surface and mineral soil was collected to a depth of one meter. The mineral soil was screened for roots and rocks and was transported by truck to Brampton for use in seedling transplanting. Additional soil collections were made in the vicinity of Plastic Lake near Dorset in May of 1987. In this collection great care was taken to remove only the acidic B horizon (5 to 30 cm depth) under the organic layer without removing the C horizon. Samples of the collected soils were analyzed for macro and micro nutrients, pH, cation exchange capacity and metals (refer to Table 1).

1.3 Acquisition and Preparation of Plant Material

Tolerance to stress can vary between individual trees among, and within, tree populations. Plant to plant variability can be controlled in a randomized block experimental design. Although genetically uniform (clonal) material is often used to clarify treatment effects, even clonal material can be variable due to differences in rooting success (Dr. H. Anderson, MNR, pers. comm.). One advantage of using seedlings rather than clonal material for the study is that the plant to plant variability parallels the variability present in natural stands.

Nursery seedling stock was desirable over natural stock because sugar maple is one of the most difficult hardwoods to transplant successfully (Morsink and Jorgensen, 1974). Transplant shock can be severe resulting in leaf deformation and discoloration and even a period of abnormal growth. Unfortunately sugar maple seedlings were unavailable from MNR nurseries in the province. Commercial nurseries could not guarantee seedling vigor or that the source of their seed was from within the province of Ontario. Propagating seedlings from germinated seed would require a waiting period of at least two to three years before seedlings of adequate size would be available. Therefore, wild sugar maple seedlings of uniform age and height (30 to 40 cm) were collected in October 1985, from a sugar maple stand located at a site near Dorset, Ontario and were transported to Brampton in bags of moist sphagnum moss (25 to a bag). Approximately 1500 bare root transplants were kept in cold storage at 4°C for two weeks and were later transplanted to 16 litre polyethylene pots containing brunisol mineral soil. Large pots were utilized to minimize root binding within the study period. Pots also have the advantage of portability and allow for the harvest of individuals from treatment plots without disturbing the root systems of neighbouring trees. Pots also eliminate competition effects in the field plots.

The potted seedlings were transplanted to a field plot near the canopy system and allowed to establish until June 1987. A plastic shade cover was erected over the maple seedlings to reduce full sunlight by 40 to 50% as in a mature stand. A soil berm was placed around the perimeter of the pots to reduce temperature fluxes in pots on the edge of the plot.

A total of 1500 nursery stock white spruce seedlings (2 yr old) were obtained from the MNR Midhurst nursery in April 1986 and were also bare root transplanted to 16 litre polyethylene pots containing brunisol soil from the maple site. These potted seedlings were also transferred to the field plot adjacent to the sugar maple seedlings and allowed to establish. Additional white spruce seedlings were obtained from the Midhurst nursery in May 1987 and were bare root transplanted to 16 litre pots containing B horizon soil collected from the second site (near Plastic Lake). These trees were placed directly into the REC treatment areas along with those white spruce seedlings which had been transplanted the previous year.

As a co-operative effort, Cuttings of fast growing hybrid poplars were obtained from the MNR Ontario Tree Improvement and Forest Biomass Institute in Maple, Ontario in June 1987. Three hybrids (DN12, DN190, OJPN105) were selected for transplanting to experimental plots along with potted sugar maple seedlings. These hybrids which grow a main stem with short side branches were included in the study to provide shade and reduce wind in the maple plots as occurs in a natural stand. They can attain a height of 2 m within the first growing season. Also, the relative sensitivity of the hybrid poplars to SAR and O₃ can be investigated and provide additional information concerning joint effects of the two pollutants on tree species.

3.2 Arrangement of Potted Seedlings in the REC Treatment Areas

Healthy sugar maple seedlings of approximately 40 cm height were removed from the establishment plots and were transplanted to the REC treatment areas in June 1987. Sugar maple seedlings were placed in the 25 field plots corresponding to the first nozzle latin square in the south end of each treatment area. The 5x5 nature of the latin squares made it necessary to assign ten replicate plots for each of the pH 4.3 and pH 3.19 treatments and five replicate plots for the pH 5.6 treatment. Prior to transfer, soil pH was measured in all sugar maple seedling pots in the establishment plot and only pots with soil pH < 6.0 were transferred to the REC plots. This provided enough sugar maple seedlings to allow four seedlings per plot for a total of 100 seedlings in each of the three treatment areas. Each pot was submerged to a depth of within 3 cm of the pot rim. They were arranged to form a square around the centre point of the plot directly under each nozzle. Sufficient space remains between the pots for the addition of up to four more pots.

After transplanting of sugar maple seedlings was complete, six hybrid poplar cuttings (two individuals of each of the poplar hybrids DN12, DN190 and OJPN105) were transplanted directly into the sandy loam soil within the perimeter of each of the sugar maple seedling plots. These poplar cuttings are subjected to the same SAR and ozone treatments as the potted sugar maple seedlings in a given plot.

A mobile PVC shade cover was suspended over the sugar maple plots during the months of June and July to provide shade until the poplars had grown to provide shade to the potted sugar maples. The shade cover was rolled back prior to each SAR application.

Soil pH was determined for potted white spruce seedlings in the establishment plot and was found to be greater than pH 6.0 in almost all

cases. For this reason, additional white spruce seedlings which had recently been transplanted to B horizon soil of pH <6.0 were utilized. White spruce seedlings were placed in the 25 field plots corresponding to the second nozzle latin square in the south end of each treatment. The number of replicate plots per treatment is similar to that for the sugar maple seedlings. In each plot, six potted white spruce seedlings were submerged to a depth within 3 cm of the pot rim and were arranged to form a hexagon around the centre point directly under the nozzle. Each plot received two seedlings which had overwintered in the establishment plot in brunisol soil with pH 6.0 to 7.0, and four seedlings which were recently transplanted into brunisol soil with pH < 6.0.

3.3 SAR and Ozone Treatment Applications

At present, regions of southern Ontario receive precipitation with an annual weighted-mean pH of 4.3 (Chan et al., 1983). One SAR treatment with pH 4.3 (50 ueq $H^+ L^{-1}$) has been selected which is representative of ambient rain in the province. A much more acidic SAR treatment with pH 3.19 (650 ueq $H^+ L^{-1}$) is being utilized to determine the potential effect of increased rain acidity. An SAR treatment with pH 5.6 (12 ueq $H^+ L^{-1}$) was also included for control purposes. The SAR treatments utilized in the REC study are produced by the addition of acid/ion stock solution to deionized water by means of metering pump. Stock solutions, contain mineral salts and H_2SO_4/HNO_3 acids based on ambient rain chemistry in southern Ontario (Chan et al., 1983) and have a final S:N mass ratio of 2:1.

During the 1987 growing season, 3 cm of SAR treatments were applied manually each week to maintain soil moisture in the seedling pots. It was felt that this would minimize the potential for drought effects which can occur when SAR applications are dependent on the frequency of ambient events. SAR was applied each week in three events at a rate of 1cm per hour per event. This amount approximates the weekly average rainfall for the past 30 years in the Toronto region. SAR applications commenced on June 23, 1987 after all transplanting to the REC plots had been completed.

The air exclusion system is activated whenever the half hour mean value of ambient ozone surpassed a 50 ppb criterion. This criterion was calculated from historical records of ozone events in the Brampton area which indicated that ambient ozone surpasses 50 ppb concentration for approximately 10% of total daylight hours during the summer months. Blowers remain on until natural precipitation occurred or the half hour mean ozone concentration fell below the specified criterion level. Ozone is generated and emitted in the blower system of the east canopy treatment area via teflon tubing into the pillows at a controlled rate sufficient to increase ambient ozone by 35 ppb in the plots. The one hour ambient air quality criterion for ozone, as written in the Environmental Protection Act of 1971, is 80 ppb O_3 . Therefore the ozone concentration in the fumigated treatment area will surpass this level whenever the blower systems are activated. Thus, the following treatment combinations are being applied to the three treatment areas:

- A) West Canopy - treatment area subjected to SAR pH 3.19, 4.30, 5.60 filtered air when ambient O_3 surpasses 50 ppb

B) Centre Canopy - treatment area subjected to SAR pH 3.19, 4.30, 5.60
ambient air only

C) East Canopy - treatment area subjected to SAR pH 3.19, 4.30, 5.60
ambient air spiked with 35 ppb O_3 when ambient O_3
surpasses 50 ppb to produce 80+ppb in plots.

It should be noted here that the ozone generator was not activated until the first week of July 1987. This was done to enable the potted seedlings and the hybrid poplars 30 days to establish before being subjected to the air pollutant.

3.4 Measurements and Observations

Several non-destructive measurements are being made on the seedlings throughout the growing season to determine direct effects,; i.e.

1. visible foliar injury rating
2. stomatal conductance with steady state porometer (Licor 1600)
3. respiration and photosynthesis rates (Licor 6200)
4. bud analysis (investigate frost hardening in spruce buds)
5. plant height, leaf number, stem diameter, leaf dimensions
6. soil leachate

Physical measurements of the tree seedlings are made at the end of each month. Foliar injury such as chlorosis, anthocyanins, necrosis and other observed injury are also assessed at this time. A Licor 6200 photosynthesis analyzer was not available for use during the 1987 growing season because the infra red gas analyzer had to be returned to the manufacturer for repairs. The study calls for photosynthesis to be measured before and after SAR applications in order to measure immediate treatment response and between events in order to measure stress recovery.

Periodically, sugar maple leaves or white spruce candles are sampled for chlorophyll and foliar uptake analyses. Leaves near the top of the plants are selected for these analyses. Soil leachate from selected spruce pots is being collected when sufficient sample is present for analysis of elemental analysis (e.g. Al and Ca).

During the second year of the study and each year after that, selected tree seedlings will be harvested. Potted trees which are removed can be replaced with new pots of same or different species each year in order to maintain replicate numbers. The following analyses are to be made on the harvested individuals:

1. chlorophyll analysis of foliar tissue
2. elemental analysis of foliar tissue
3. investigate internal changes to cell size and shape
4. investigate physical and chemical changes to roots
5. electrophoresis
6. integrity of cuticle
7. analysis of sugars, proteins, starches etc.

Each day environmental parameters are recorded continuously on the site. Thermohydrographs mounted in stevenson screens in the centre of each treatment area monitor changes in temperature and humidity at all times. Modifications to micro-climate during periods when the canopies are over the

plots can be detected in this way. Soil water potential is monitored by tensiometers distributed randomly in various seedling pots in the three treatment areas (eight per canopy). As backup to the tipping bucket rain gauge, ambient rain is also recorded by two rain collector gauges and a chart recorder gauge. Rain chemistry is determined from ambient rain samples collected from a Sangamo electronic wet/dry deposition collector located on the roof of the control trailer (e.g pH, total acidity, conductivity, SO_4 , NO_3 , PO_4 , NH_3 , Ca, Mg, Na, K, Cl).

2. Indoor Experiment using greenhouse and chamber facilities

During September 1986, selected sugar maple and white spruce seedlings were transplanted to 6 litre pots containing either medium screened garden loam or brunisol soil (from the Dorset site). The potted seedlings were maintained in a garden plot until January 1987 at which time they were brought into the west greenhouse of the MOE Phyto laboratory. The sugar maple seedlings began to crack dormancy by mid February. The white spruce seedlings began to generate new shoots almost immediately.

All the seedlings were maintained on elevated benches inside a greenhouse with automatic temperature and humidity control. Pot positions were randomized after each treatment application. Temperature was maintained at 22/18°C day/night and humidity was approximately 50%. In addition, the greenhouse was supplied with charcoal-filtered air to reduce background gaseous pollutants in the ambient atmosphere. Supplementary light in the form of fluorescent and incandescent lamps providing a photon flux density of $350 \mu\text{E m}^{-2}\text{s}^{-1}$ extended the photoperiod to 14 hrs. All pots received supplemental irrigation with deionized water as required.

For each of two unamended soil types (brunisol from Dorset and garden loam) there were five replicate sugar maple seedlings and three replicate spruce seedlings. All seedlings were exposed to the following treatments: pH 4.3 (50 ueq); pH 3.34 (450 ueq); O_3 alone (100 ppb peak); $4.3 \times \text{O}_3$; $3.34 \times \text{O}_3$; green house controls. In addition, Soil in pots of one set of replicates was amended with phosphate (0-20-0) fertilizer). These plants were exposed to SAR $3.34 \times \text{O}_3$. This was done to determine if PO_4 fertilizer would provide available P (a limiting nutrient in soils) to the trees and to determine if P fertilizer reduces Al availability in the soils which can be phytotoxic under acid conditions.

Solutions of SAR were made from additions of reagent grade H_2SO_4 and HNO_3 to deionized water and a S:N mass ratio of 2:1 was maintained. Background ions typically present in ambient precipitation occurring in southern Ontario were added as mineral salts (refer to Table 2).

During the period of March 6 to April 28, 1987, SAR was applied to the maple and spruce seedlings three times per week (Mon, Wed, Fri) in four specially designed indoor rain chambers (Enyedí and Kuja, 1986). Treatments were rotated amongst the chambers each week. SAR treatments were applied over an eight week period for a total of 20 events. SAR application rate was 0.8 cm per event for a 40 minute duration. Chamber temperature and humidity was recorded prior to and after each event. Ozone fumigations were applied in chambers two times per week (Tues, Thurs). Seedlings in garden loam were treated on one day, seedlings in Dorset soil were treated on the other day such that each treatment rep was exposed to a total of six

fumigations. Ozone was applied for 7 hours with a peak of 100 ppb (0 - 100 ppb). Chamber conditions were kept at 20 to 22°C and humidity of 75%. SAR plants not receiving O₃ were placed in a control chamber of the same temperature and humidity during the exposure period to determine chamber effects.

Physical measurements were made on a bi-weekly basis. Foliar injury (chlorosis, necrosis, etc.) was also assessed. Stomatal conductance of sugar maples was measured with a Licor 1600 steady state porometer immediately after each ozone fumigation while plants were still in their respective chambers. Measurements were made on second set of leaves. At the end of the experiment, leaves of all spruce and maple were collected for elemental analyses (S, N, P, K, Ca, Mg, Al, Fe, Mn, Pb, Zn, Ni, Cu, Cd, Na, Mo, Cl) were performed. Leaf discs were removed from the second set of leaves on all maple seedlings, and needles were removed from the apical stem of spruce seedlings, were frozen and later analyzed for chlorophyll. Chlorophyll was extracted using methanol and peaks of Chlorophyll a and b were determined on a Bausch-Lomb scanning spectrophotometer.

RESULTS AND DISCUSSION

A total of 331.4 mm of ambient rain fell during the period of June 23 to September 30, 1987 with pH ranging from as low as pH 3.69 to as high as pH 5.6. During this time a total of 324 mm of SAR was applied in 36 events. Even though SAR was applied in predetermined amounts each week, the total amount was very close to the ambient total rainfall during the same period. Ambient ozone exceeded the 0.05 ppm level on 26 occasions. The highest ambient ozone concentration was 101 ppb (on August 15). The air exclusion was operated for a total duration of 102.5 hrs. Plots in the east treatment area were exposed to controlled ozone fumigations whenever blowers were activated.

To date, physical measurements made on both sugar maple seedlings and white spruce seedlings in the three REC treatment areas during the initial summer of the REC field study show no significant treatment effects (i.e. stem diameter, plant height, apical length, number of leaves or candles, branch or candle length, colour). Physical measurements were quite variable between test plants within experimental plots. The high plant to plant variability may be attributed to varying degrees of transplant shock resulting from transfer to the REC plots. Only a third of the white spruce seedlings in the REC plots had overwintered in an establishment plot. Sugar maple seedlings showed wind damage to leaves from wind which occurred prior to transfer to the REC plots. It is likely that treatment effects can be better determined during the second year of the study after the test plants have had more time to establish.

Total chlorophyll content of sugar maple leaves sampled from the REC plots on Sept. 8, 1987 is shown in Figure 2. This sample was collected relatively late in the growing season but the leaves showed no sign of autumn coloration. Although there was no significant difference among treatments ($P > 0.05$), the pH 5.6 treated leaves tended to have higher chlorophyll content than the leaves from the other two treatments. This trend may prove to be significant in subsequent years.

The preliminary greenhouse experiment was conducted in March and April

1987. This two month period was considered too short to establish conclusive results. Nevertheless, significant effects were noted due to soil type and ozone fumigation (figures 3 to 8).

The seedlings grown in the Dorset soil had significantly greater basal diameters and chlorophyll contents. The greatest difference was in the chlorophyll content as shown in Figure 3. The two soils have similar chemistry but vary considerably in texture (Table 1) which may be the factor responsible for the differences. There was no significant treatment effect; however, the pH 3.2 sprayed leaves had consistently higher chlorophyll contents than the pH 4.2 treated leaves. This was unlikely caused by direct foliar contact because simulated acid rain has been shown to decrease chlorophyll content and cause necrotic lesions (Evans *et al.*, 1977). The acidity may increase the mobility of nutrients in these neutral soils and thus increase the availability of nutrient cations such as calcium and magnesium to these seedlings.

The simulated acid rain and ozone treatments had no significant effect on the overall height, apical growth, side branch growth, number of leaves, leaf area or basal diameter of the sugar maple seedlings. Figure 4 and 5 show the increase in height of seedlings sprayed with SAR with pH 3.4 and 4.2 during the period of March 12 to April 23, 1987.

The high variability and low growth obscure any trends which may emerge over a longer period of time. The opposing pattern of growth due to treatment for the two soils underlines the importance of the choice of soil (even of the same pH) on SAR effects. The ongoing study in the outdoor REC system includes seedlings potted in 'Dorset' soil, with a pH from 5.5 to 6.0 or a B horizon soil with a pH <5.5, and will include seedlings taken directly from a forest stand with their natural soil profile intact. This should help to clarify the interaction of soil and simulated acid rain effects on sugar maple seedlings.

Figure 6 shows the foliar calcium content of sugar maple seedlings treated with simulated acid rain and ozone. This figure indicates an interaction between the two pollutants. The highest calcium content was found in leaves of seedlings exposed to SAR alone; the lowest content was in those exposed to both SAR and ozone. The pH 4.2 sprayed seedlings showed consistently higher foliar calcium contents compared to those sprayed with pH 3.4 SAR (Figure 6). These differences may be attributed to foliar leaching. Figure 7 shows that foliar leachates from sugar maple seedlings subjected to pH 3.4 SAR had higher calcium, potassium and to a minor extent magnesium concentrations than those which received pH 4.2 SAR. This cation loss resulting from leaching by SAR has been well documented (Fairfax and Lepp, 1975) and may lead to nutrient deficiencies in sites with poor nutrient soils (Zoettl and Huettl, 1986). Ozone fumigation can increase foliar leaching due to erosion of the cuticle and direct foliar damage (Karhu and Huttunen, 1986).

Stomatal conductance of leaves can be an indicator of stress which might result in reduced growth or vigor due to both SAR and ozone. Stomatal conductance in leaves of sugar maple seedlings was adversely affected by exposure to ozone (Figure 8). The seedlings fumigated with ozone alone and those subjected to pH 3.4 SAR and ozone had significantly less conductance than the plants sprayed with pH 4.2 SAR. The phosphate fertilizer appears to ameliorate the negative effects of the ozone and SAR effects.

SUMMARY

The results of the indoor and outdoor studies show no significant effects due to simulated acid rain. Seedling response to ozone was minor. This is due to a large extent to the short duration of the indoor experiment and outdoor study to date. Significant growth reductions could not be determined for the relatively slow growing sugar maple seedlings because of large plant to plant variability. Exposure to ozone fumigations consistently showed deleterious effects as demonstrated in reductions in foliar chlorophyll content, foliar calcium content and stomatal conductance.

SAR with pH 3.4 may increase the mobility of nutrients in the soil which could result in an increase in chlorophyll content. However, this effect is closely related to the type of soil used. Increased foliar leaching of elements such as calcium may prove injurious to plants grown on soils of low nutrient status and limited nutrient cycling. The soils used in the preliminary experiment were not acidic nor were they deficient in base cations. These soils were not likely sensitive to increased mobilization of aluminum by SAR. The soil in which test plants are grown is clearly a factor which warrants further investigation in the ongoing REC study.

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Table 1. Chemistry of soils utilized in the greenhouse and REC study

Soil Parameter	'Dorset Soil'	'Garden Loam'
pH	6.4 - 7.0 [*]	7.7
N (mg/g)	14.9 ±3.2	11.4 ±.9
P (mg/g)	0.9 ±.12	1.38 ±.54
K (mg/g)	0.48 ±.09	0.55 ±.01
Ca (mg/g)	18.4 ±1.5	16.8 ±3.4
Mg (mg/g)	3.1 ±.47	3.4 ±.24
Al (ug/g)	13.6 ±2.3	17.3 ±3.0
Fe (ug/g)	62.4 ±14.9	50.5 ±10.8
Zn (ug/g)	20.4 ±5.8	20.0 ±5.9
% Sand	90	60
Silt	7	20
Clay	3	20
% Org. Carbon	4	10

^{*} B horizon soil collected at 'Plastic Lake' site had pH 4.5 to 5.7

Table 2. Chemical composition of simulated
acidic rain (SAR) solution

Acid levels of simulated rain solutions *				
SAR	H^+ ueq L^{-1}	pH	Acid vol. $mL L^{-1}$	
			H_2SO_4	HNO_3
1	12	5.60	0	0
2	50	4.30	1.001E-3	8.849E-4
3	450	3.35	9.003E-3	7.962E-3
4	650	3.19	1.301E-2	1.151E-2

* All simulated rain solutions contained the following
background ions ($mg L^{-1}$):

K - 0.063 $mg L^{-1}$, Ca - 0.501 $mg L^{-1}$,
Mg - 0.103 $mg L^{-1}$, Na - 0.100 $mg L^{-1}$,
 NH_4 - 0.744 $mg L^{-1}$, Cl - 0.023 $mg L^{-1}$,
 SO_4 - 2.771 $mg L^{-1}$, NO_3 - 1.385 $mg L^{-1}$,
S/N ratio - 2.0:1.0

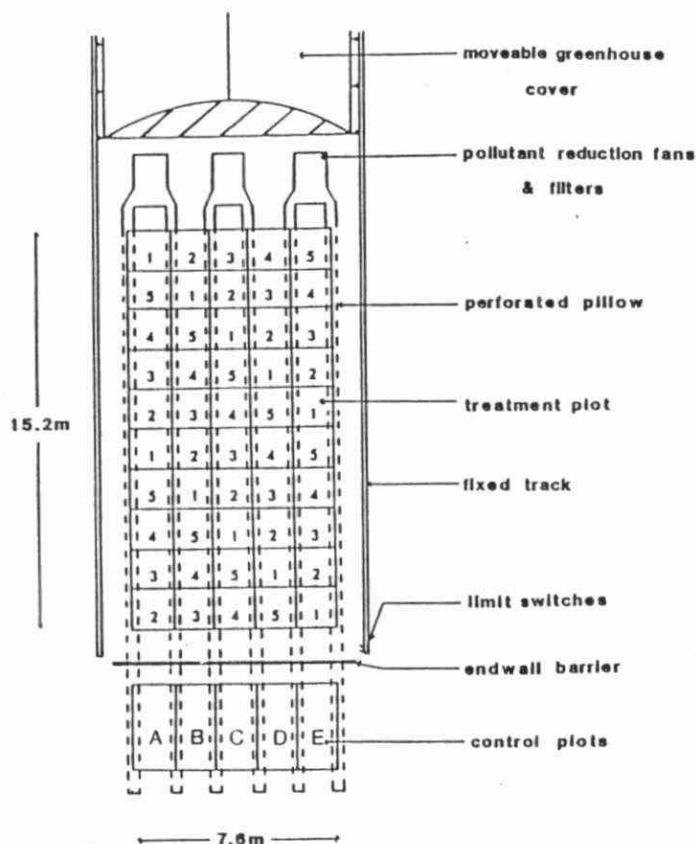


Figure 1. Precipitation Exclusion and Gaseous Pollutant Reduction System (only one system is shown for clarity).

Fig. 2: Total Chlorophyll Content of
Sugar Maple Leaves Treated with SAR

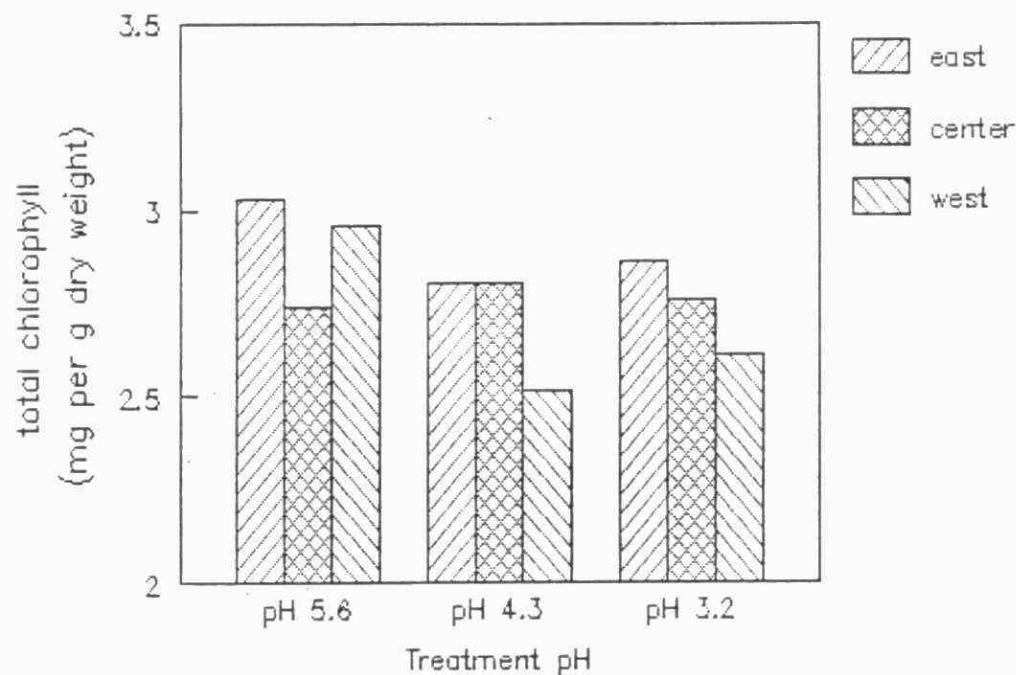


Fig. 3

Chlorophyll Content of Sugar Maple Seedlings
Exposed to Simulated Acid Rain and Ozone

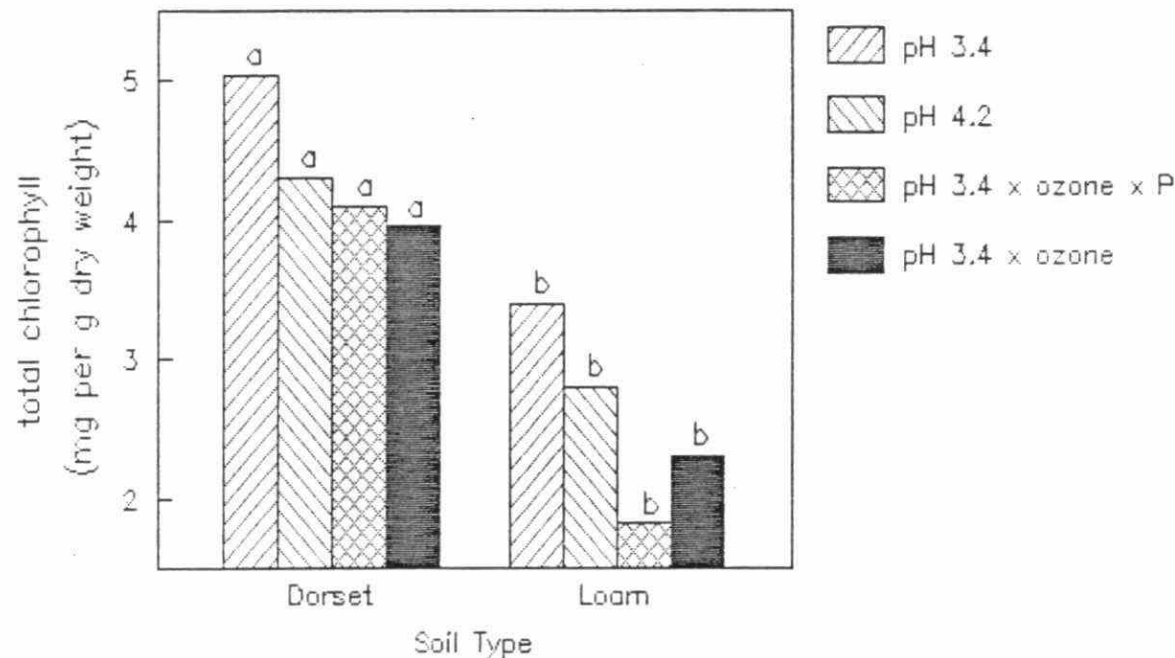


Fig. 4:

Relative Height of Sugar Maple Seedlings in
Loam Soil Treated with Simulated Acid Rain

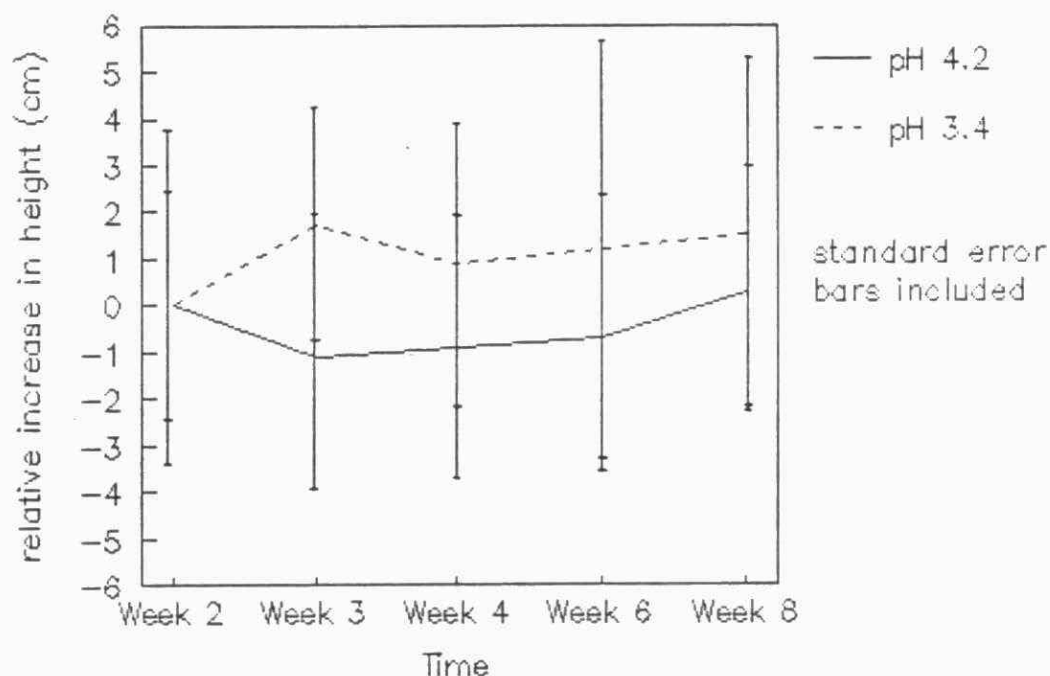


Fig. 5:

Relative Height of Sugar Maple Seedlings in
Dorset Soil Treated with Simulated Acid Rain

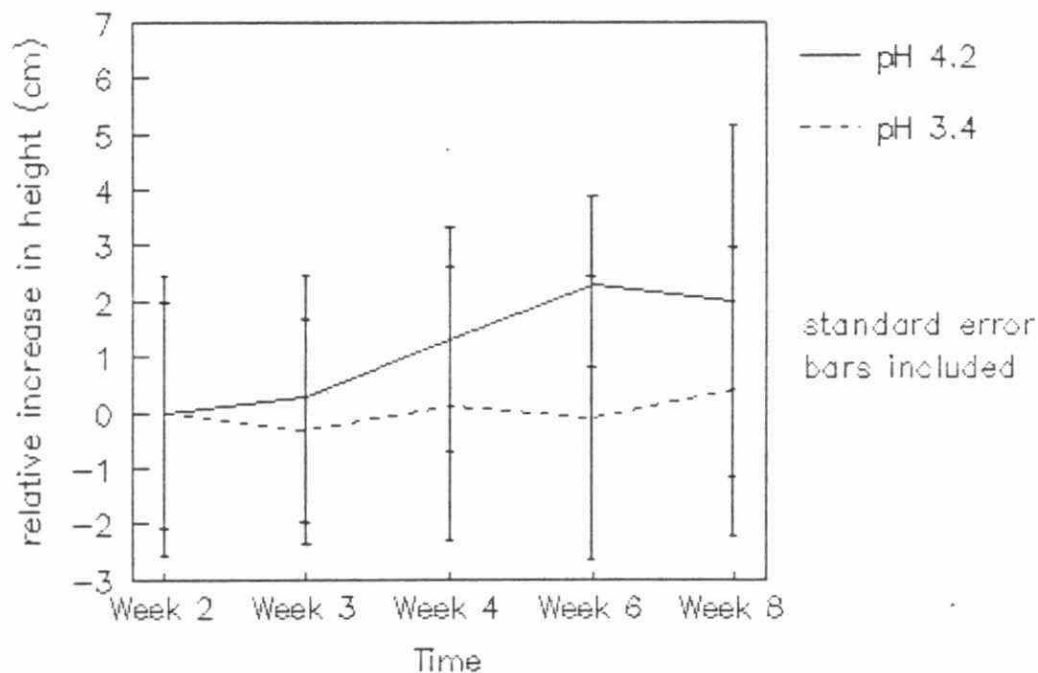


Fig. 6: Calcium Content of Sugar Maple Seedlings
Treated with Simulated Acid Rain and Ozone

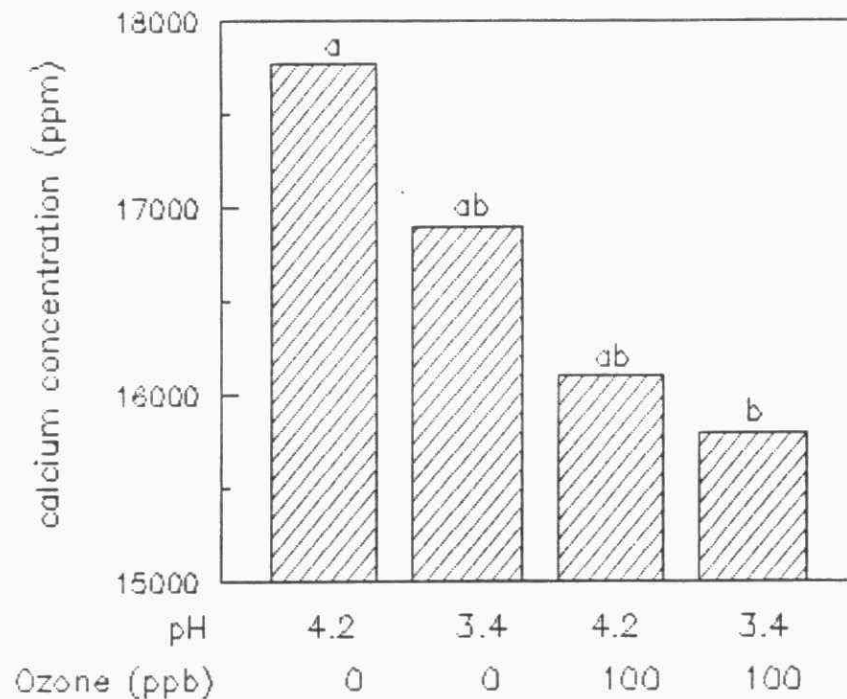


Fig. 7:

Leachate from Leaves of Sugar Maple Seedlings
Treated with Simulated Acid Rain

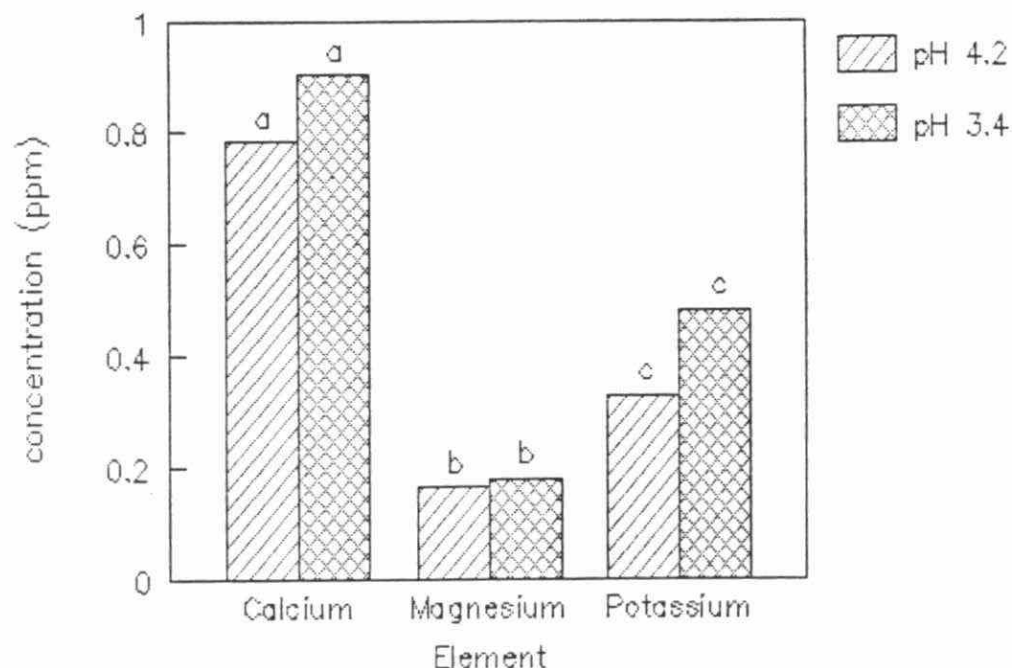
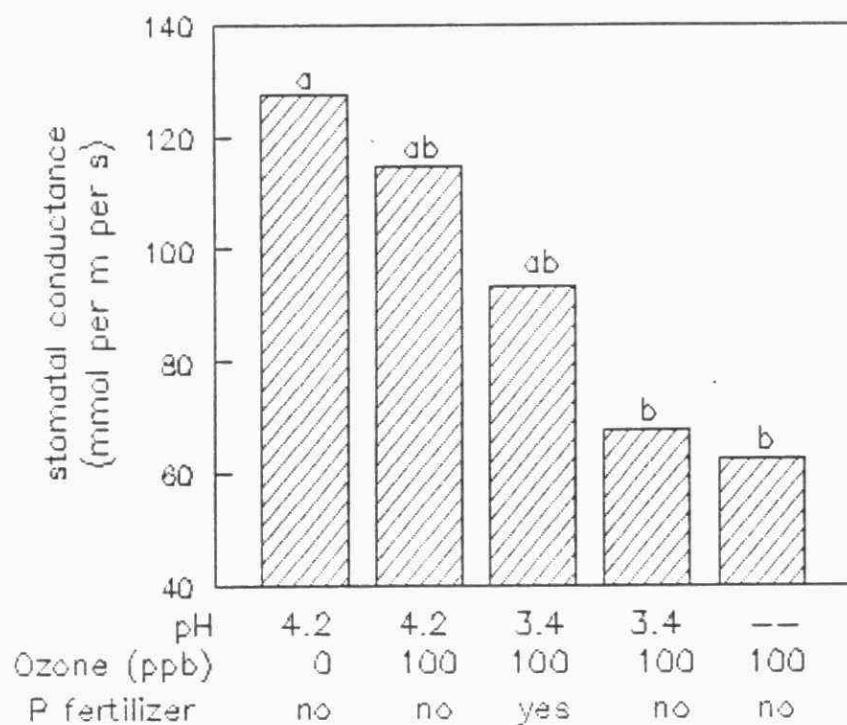


Fig. 8: Stomatal Conductance of Sugar Maple Seedlings
Exposed to Simulated Acid Rain and Ozone



MONITORING ENVIRONMENTAL GENOTOXICITY USING
SISTER CHROMATID EXCHANGES AND MICRONUCLEUS INDUCTION
IN HOUSE MICE

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INTRODUCTION

Several years ago I proposed the need for a monitoring system which would provide us with an EARLY WARNING ON GENERAL CHANGES IN ENVIRONMENTAL GENOTOXICITY LEVELS (Petras et al, 1983). This proposal involved either using organisms native to the regions or sites of concern, or placing organisms in enclosures at these sites. The locale for this study was southwestern Ontario. Southwestern Ontario is well suited (unfortunately) because individuals living in this area are subject to an onslaught of a broad range of man-made pollutants including agricultural pesticides, automotive exhausts, industrial emissions, waste incineration products. The organism I proposed using was the house mouse, Mus domesticus. The mouse was selected because of its ubiquity not only in the study area but throughout the world, its use in mutagenicity studies under laboratory conditions, its ease of maintenance and handling, and its evolutionary relationship to man. The assay originally proposed was the in vivo SISTER CHROMATID EXCHANGE (SCE) TEST using mouse bone marrow cells. The SCE test was selected because of its sensitivity and a strong correlation between SCE induction and carcinogenesis (Abe and Sasaki). Subsequently we began looking for a second assay partly to substantiate and partly to complement the SCE findings. For reasons given below an assay involving MICRONUCLEATED (MN) ERYTHROCYTES IN PERIPHERAL BLOOD was selected.

Although the SCE studies in mice are continuing, because of the time, this presentation is concerned primarily with the use of the MICRONUCLEUS ASSAY in monitoring the environment for genotoxicity. Factors which could affect the reliability of the MN assay in peripheral blood erythrocytes, attempts to improve the sensitivity of the test, and data obtained from surveying natural populations of house mice are examined. MN and SCE data of mice collected from

natural populations are compared. Finally, preliminary results on the usefulness of two other rodents, the deermouse, Peromyscus maniculatus, and the meadow vole, Microtus pennsylvanicus, are also presented.

THE MICRONUCLEUS ASSAY

General Characteristics

Although it has been considered to be slightly less sensitive than the SCE assay by some (Bauknecht et al, 1977; Lasne et al, 1984; Tice et al, 1987), the MICRONUCLEUS ASSAY FOR PERIPHERAL BLOOD ERYTHROCYTES (MN-PBE assay) was selected as the second monitoring system because it has been described as simpler, faster and easier to score than other cytological monitors of genotoxicity (Heddle, 1973; Salamone and Heddle, 1983). Typically micronuclei have been assayed in polychromatic cells (PCEs) of bone marrow. These occur as the penultimate stage in erythrocyte formation. Tice and Ivett (1985) in summarizing the positive features of the bone marrow micronucleus assay pointed out that: a) micronuclei can be identified quickly in anucleated polychromatic erythrocytes, b) metaphase preparations are not required since interphase cells are used, c) newly formed cells reside in bone marrow only about 24 hours and, therefore, any increase in micronucleated polychromatic cells is an indication of a recent exposure to a mutagen, and d) there is a strong correlation between cancer induction and micronucleus induction. Furthermore, the MN assay has been considered complementary to the SCE assay because MN and SCE inductions appear to be independent (Renault et al, 1982). The drawbacks of the bone marrow assay include lower sensitivity, some DNA-nonrelated causes of micronuclei and the inability to do sequential sampling since animals are killed to assay bone marrow material.

To overcome the last problem MacGregor et al, (1980) suggested assaying

for micronuclei in polychromatic (PCEs) and normochromatic erythrocytes (NCEs) of peripheral blood and therefore sacrificing of the mice is not required. This approach also permits distinguishing between recent and longterm or chronic exposure to a mutagen since PCEs survive as such for only about 48 hr in peripheral blood and NCEs may last up to 50 days. Counts of MN-NCEs are reliable in the mouse because, unlike the situation in rats and humans, micronucleated cells do not appear to be preferentially removed from peripheral blood of this species (MacGregor et al, 1980; Schlegel and MacGregor, 1982).

The above properties make the MN-PBE assay especially valuable in studies of natural populations, in continuous monitoring of long term exposures and in genetic analyses. The usefulness of the MN assay was further enhanced by the use of an acridine orange [494-38-2] fluorescent staining technique first described by Hyashi et al (1983). This procedure appears to eliminate many of the scoring problems associated with Giemsa.

Laboratory Procedure

The staining procedure used in this study was obtained from R.R. Tice (personal communication). The following steps are involved: a) peripheral blood is collected by inserting a heparinized tube into the suborbital sinus of the mouse; b) a drop of blood is spread evenly on the microscope slide; c) the slide is air dried and fixed in absolute methanol for 15 minutes; d) after 24 hours of aging the slide is stained with acridine orange (0.06125mg/ml phosphate buffer, pH 7.4) for 3 to 4 minutes, then rinsed and washed in the buffer for 6 minutes; e) the spread is covered carefully, to avoid air bubbles, with a cover slip; f) the slide is then examined under fluorescence microscopy (FITC filter combination, excitation wavelength 495nm, emission wavelength 520nm) and scored for i) number of micronucleated normochromatic erythrocytes

(MN-NCEs) in 1000 NCEs, ii) number of micronucleated polychromatic erythrocytes (MN-PCEs) in 1000 PCEs, and iii) percentage of PCEs in 1000 erythrocytes.

The scoring of micronucleated cells is relatively straightforward because acridine orange discriminates between DNA which fluoresces green and RNA which fluoresces red (Hayashi et al, 1983). As a result, under fluorescence, micronuclei which have been stained with acridine orange appear green, NCEs brownish-green and PCEs reddish-orange. If either the fluorescence or background colour are not suitable, a slide can be destained with absolute methanol and restained.

RELIABILITY OF THE MN ASSAY

Maximization of Assay Efficiency

In an effort to make the MN-PBE assay as efficient as feasible, a time profile of micronucleus induction was developed for three mutagenic compounds, cyclophosphamide (CP), methyl methanesulfonate (MMS) and mitomycin C (MMC). These compounds were selected because they have different time profiles in inducing micronuclei in bone marrow cells (Hayashi et al, 1984; Salamone et al, 1980).

CP (50mg/kg), MMC (2mg/kg), MMS (50mg/kg) or isotonic saline were injected once, intraperitoneally, into four, five month old C3H male mice. Blood samples were taken from the suborbital sinuses. The first samples were taken just before injection and then at 12 hr intervals beginning 24 hr after injection and ending 72 hr later. The last blood samples were taken 23 days after the first to see if the micronucleated cells returned to the starting levels.

For all three mutagens the maximum number of PCEs was observed around the

48 hr mark (Table 1). This is about 24 hr later than in bone marrow cells for the MMC and MMS treated mice (Hayashi, 1984) and 12 hr later for CP treated animals (MacGregor et al, 1980). A slight increase of micronucleated NCEs appeared to occur 24 to 48 hr after the MN-PCE peak. The increase of MN-NCEs is not expected to be as great as that of MN-PCEs because of the dilution of newly matured MN-NCEs. Since NCEs are estimated to have a lifespan of from 35 to 50 days, the effect of a single injection is diluted at least ten-fold. Calculations based on the MN-PCEs observed would suggest that from a single injection, at the concentrations used, the maximum MN-NCE count should be about 3 (Hayashi et al, 1984).

During the time response study, information on the percent of PCEs observed in peripheral blood was also collected (Table 1). This is a measure of new PCE production. In the controls the percent of PCEs increased with each 12 hr bleeding session. The production of erythrocytes appears to be stimulated by the removal of blood. In mice injected with 50mg/kg CP the same pattern was observed but the production of new PCEs was reduced by almost 50%. A 200mg/kg dose of CP almost completely inhibited new PCE production in the house mouse (see Table 2). MMC even at 2mg/kg also greatly reduced new PCE production. MMS at 50mg/kg appeared to have almost no effect. By the 23rd day the PCE levels were almost back to the pretreatment values in all three groups.

This phase of the study suggests that mice should be examined about 48 hours after their exposure to a mutagen. Wild mice should, therefore, be examined for micronuclei in peripheral blood PCEs within 48 hours of being trapped. Also if the exposure to a genotoxic agent was short-term, that is a single pulse, then the MN-NCEs should not increase much over background level.

Short-term (acute) Exposure and MN Induction in Splenectomized Mice

In an attempt to increase the sensitivity of the MN assay in peripheral blood and since the spleen is generally considered the organ which removes abnormal erythrocytes from peripheral blood, CP was also injected into splenectomized animals. Mice injected with isotonic saline served as controls. The findings, involving two inbred strains of mice, C3H and BALB/c, are summarized in Table 3.

Removal of the spleen in the two strains and subsequent injection with isotonic saline two weeks later did not seem to have a significant effect on the frequencies of MN-PCEs, MN-NCEs and total PCEs in peripheral blood. Injection of 50mg/kg CP into splenectomized C3H and BALB/c mice appeared to have the same effect as it did in intact mice. There was a substantial increase in MN-PCEs 48 hr after injection. The magnitude of that increase was similar to that observed in intact mice (see Table 1). Even the percent PCEs in the blood stream after six bleedings was similar in intact and splenectomized mice.

Splenectomy therefore had no effect on PCE levels in the house mouse after a single exposure to CP.

Effects of Multiple Exposures to CP on MN Induction

Multiple exposures of animals to a mutagen simulate chronic exposure conditions. The objective was to determine whether multiple injections of CP would increase the incidence of MN-PCEs, of MN-NCEs and percent PCEs in peripheral blood over that observed after a single injection. Schlegel and MacGregor (1982) and Salamone and Heddle (1983) suggested that on chronic exposure to a mutagen the frequency of MN-NCEs should increase and should persist even after the exposure. Furthermore, as mentioned earlier, since the

spleen is involved with both the synthesis and the removal of erythrocytes, does splenectomy affect any of the parameters on injection with either saline or CP.

Table 4 summarizes the effects of multiple injections of CP on splenectomized and intact C3H mice. At the outset injections of CP or isotonic saline were given twice a week. After day 15 this was changed to three per week. Bleeding was usually done every Monday except in those instances where information was sought about the levels of MN cells 48 hr after injection.

As has already been shown saline did not increase the MN erythrocytes in C3H. CP on the other hand increased the MN-PCEs in C3H so that by day 21 and 48 hr after an injection a MN-PCE level of approximately 25 MN-PCEs/1000 PCEs was reached. A similar value was observed whenever an injection of CP preceded the bleeding by 48 hr. By 21 days a similar value of MN-PCEs was reached in splenectomized C3H mice. The value went up to 36/1000 by day 30.

The MN-NCEs also increased in number with chronic exposure of the mice to CP. In both intact and splenectomized mice CP increased the levels to between 10 and 16 MN-NCEs/1000 NCEs. If the spleen does not preferentially remove MN cells then the level of MN-NCEs can be predicted from the MN-PCEs that are observed in the 30 to 50 days prior to the MN-NCE determination. In C3H the MN-NCE levels observed were consistent with the hypothesis that the spleen is not removing MN cells preferentially. The observed fluctuations in the MN-NCEs were probably due to the bleeding and treatment schedules and the frequency of MN-NCEs would probably stabilize in the mice if they could survive daily injections of CP.

The CP treatment appeared to affect the percent PCEs in peripheral blood of splenectomized C3H animals to a greater extent than of intact mice. Splenectomized C3H mice also appeared to be more sensitive to the physiological

effects of CP than were intact mice. The former survived about half the length of time that the latter did, 35 days vs. 80.

Based on the time over which a 'steady state' level was reached in MN-NCEs the lifespan of the NCEs appears to be about 30 days.

The BALB/c chronic exposure data are summarized in Table 5. Again splenectomy appeared to have no effect on MN-PCEs. Both intact and splenectomized BALB/c mice were more sensitive to CP than were C3H animals. Chronic exposure to CP resulted in an increase of MN-NCEs as in C3H except that the steady state level is somewhat higher to correspond with the higher induction of MN by CP in this group. The lifespan of the NCEs appeared to be similar to that determined for the C3H animals.

In both C3H and BALB/c mice, chronic exposure increased MN-NCE levels and there appeared to be no selective removal of MN-NCEs by the spleen. Splenectomy had no effect on any of the parameters used.

Effects of Bleeding on MN Erythrocytes

Steinheider et al (1986) reported that bleeding of mice affected the frequency of MN-PCEs in peripheral blood. To determine the magnitude of this effect two experiments were done. In the first, three different volumes of blood were taken in a single bleeding (Table 6) and in the second after taking 0.5ml in the first bleeding, 0.06ml were taken in subsequent bleedings. These are the amounts usually taken in a long term bleeding schedule (Table 7).

Table 6 shows that as the amount of blood removed was increased the frequency of MN-PCEs also increased. This increase of MN-PCEs was significant ($P = 0.05$) for both 0.50ml and 0.75ml of blood.

In the multiple bleeding experiment (Table 7) a significant increase in MN-PCEs was seen on the fourth bleeding ($P = 0.01$). The effect was reduced by

the fifth bleeding but it was still significant ($P = 0.05$). The reason for the decrease in MN-PCEs at the fifth bleeding is not obvious. Perhaps the animals are adjusting physiologically.

In monitoring the environment using the MN-PBE assay care must be taken not to remove large quantities of blood at any one time if subsequent bleeding and MN assaying is to be done. If multiple bleeding is necessary then a week should separate the bleedings and no more than one hematocrit tube full should be taken at each bleeding.

Sex and MN Induction in Wild Mice

Table 8 summarizes an experiment in which wildcaught mice, housed in the laboratory for at least two weeks, were given 50mg/kg CP. Forty-eight hours later they were examined for MN-PCEs in peripheral blood. Comparison between the sexes showed no significant difference in MN induction. Since this was consistent with results obtained in C3H and BALB/c mice, data for the two sexes were pooled in all subsequent studies.

Age and the Induction of Micronuclei

Reimer et al (1985) reported that age had a significant effect on the induction of micronuclei in bone marrow cells. They suggested that older mice perhaps because of a reduction in DNA repair efficiencies showed higher MN-PCE counts on exposure to a mutagen than younger animals.

Since mice brought in from the wild are of unknown age and can be readily classified only as juveniles (18 to 35 days), young adults (35 to 60 days) and adults (60+ days) this could present a problem. Offspring of wild mice whose ages were known were given 50 mg/kg CP and examined for MN 48 hr later. Mice of inbred strain, C3H and BALB/c, served as standards. Table 9 shows that the

three age groups of wild offspring did not differ significantly from one another either before or after treatment and also that they did not differ from the inbreds.

Table 10 presents results of MN induction by CP for a large sample of wildcaught mice. The 1987 mice were housed under laboratory conditions for at least two weeks prior to testing and the 1986 sample at least 12 months. Juveniles and adults collected in 1987 gave almost identical MN-PCE values and even wild mice differing in age by almost a year did not respond differently to CP.

There appears to be no reason to be concerned about the age of wild mice to be used in the MN-PBE assay.

Genetic Heterogeneity and MN Induction

Yet another concern regarding the reliability of the MN-PBE assay was the effect that genetic variability had on MN levels. There is ample evidence from electrophoretic studies that mouse populations in general (Selander and Yang, 1969; Berry, 1977; Bonhomme and Selander, 1978) and the population in southwestern Ontario in particular (Petrus et al, 1969) are highly polymorphic. Such genetic variability could extend to loci controlling the pathways responsible for the detoxification of genotoxins, DNA repair, etc. and so could reduce the reliability of the test.

To test this possibility a comparison was made between the responses of mice belonging to the inbred strain BALB/c and of mice collected from a number of sites in southwestern Ontario in the summers of 1986 and 1987.

The results of the MN-PCE levels observed at 0, 48 and 72 hr post-injection are presented in Table 11. The MN frequencies in PCEs and NCEs and their variances were very similar in both inbred and wild mice. Barlett's

test of homogeneity of variances showed that the variances of the three groups were not significantly different.

Obviously this study should be expanded to more mutagens. Based on CP data, genetic heterogeneity in wild mice does not appear to affect the reliability of the MN-PBE assay.

NATURAL ROUTES OF MUTAGEN INTAKE

Effects of Mutagens in Drinking Water

Generally studies done in the laboratory involve intraperitoneal injections of the chemicals to be tested. This phase of the work was concerned with introducing a mutagen into an animal via the digestive tract and is an extension of an earlier study. One reason for repeating this study was to provide a comparison between SCE and MN assays and to determine whether the latter was sufficiently sensitive to detect the effects of recent and chronic exposures to the mutagens of concern.

Mice were exposed to various concentrations of methyl methanesulfonate and cyclophosphamide as well as sugar water (20g glucose/l water) and tap water. Glucose had been added to the water in which the mutagens had been dissolved to make the solutions more palatable. Without the sugar the mice, especially at higher concentrations of the mutagens, were drinking very little and as a result were becoming seriously dehydrated. The sugar was effective although at the highest doses of the mutagens some mice still had to be sacrificed because of considerable weight loss. Table 12 shows that mice fed on 60mg/100ml MMS and both 118 and 236mg/100ml CP showed significant increases in MN-PCEs after 15 days of exposure. No comparable increases were, however, seen in the MN-NCEs. This is especially evident with the CP treatment where, based on earlier findings involving injections, the expected MN-NCEs should have been

about 10.

Table 12 also gives a comparison between the results of the MN assay and SCE analyses. There appears to be better correlation between dose and the SCE counts than between dose and MN levels. The difference between sugar water and tap water was not significant. The differences between the treatment groups and the controls were significant ($P = 0.05$) for all concentrations except for the lowest dose of MMS.

Mutagens in drinking water can increase MN-PCEs if the concentration used is adequate. There is no obvious explanation for the low MN-NCEs counts. This experiment will be repeated with splenectomized mice.

Effects of Benzene Inhalation on Induction of Micronuclei

A second set of experiments to evaluate the induction of micronuclei in erythrocytes by mutagens delivered by a natural route involved the inhalation of benzene.

The first phase was concerned with determining the concentrations of benzene that would cause a distinct but modest increase in MN-PCEs in BALB/c mice without debilitating the animal. The mice were exposed to benzene by dropping a measured amount of benzene on the bedding in a corner of a covered cage placed in a fumehood. This was done hourly beginning at 10:00 a.m. and ending at 4:00 p.m. each day and continued for a designated number of days. In intact animals only a dose of 0.50ml benzene had a significant effect on the frequency of MN-PCEs. Animals which had their spleens removed surgically two weeks before treatment showed a slight increase in MN erythrocytes in both controls and animals exposed to 0.25ml benzene per hour. Sham animals, animals which were subjected to the same surgical procedure as the splenectomized mice but did not have their spleen removed, also showed an increase in MN-PCEs over

the intact controls. No increases were seen in MN-NCEs but this is not unexpected because of the short exposure time.

To determine whether inhaled benzene could cause an increase in MN-NCEs BALB/c mice were exposed to 1.0ml of benzene over a 16 day period. The results are given in Table 14. In this experiment the MN-PCEs increase exceeded 50/1000 PCEs at around the seventh day and then dropped to around 29/1000 by day 11. The MN-PCEs stayed at this level until two days after the cessation of treatment. As expected with long term exposure an increase in the MN-NCEs was also observed. The MN-NCE count appeared to level off at about 13/1000. This is consistent with the input of MN-PCEs and a 30 day lifespan for NCEs. The production of new PCEs did not appear to be affected drastically by benzene.

NATURAL POPULATIONS

Micronuclei and Natural Populations

Since sex, age and genetic heterogeneity did not affect the sensitivity of wild mice to CP, wild mice collected from corn cribs in the summers of 1986 and 1987 have been and are being tested for MN erythrocytes and the frequency of PCEs within 48 hr of being caught. Table 15 summarizes the MN values observed in wild mice collected in the summer of 1986. Comparable data are being accumulated for the summer 1987 collections. Very little variability was observed; no temporal or geographic patterns were evident. The MN results are unlike those observed with the SCE assay. Not only did the SCE assay show both seasonal and geographic variability but in fact such variability has been observed since 1983 (Table 16). Although these patterns do vary somewhat from year to year generally the populations from the western part of the distribution gave higher SCE values than those from the eastern region and the

SCE counts during the spraying period were higher than those seen prior to or after spraying. The variations in frequencies, although statistically significant were relatively subtle. No major shifts were observed in any of the samples.

The data on natural populations of mice suggests that the MN-PBE assay may be less sensitive than the SCE analyses and as a result may not be useful for monitoring subtle fluctuations in genotoxin levels.

OTHER RODENTS

Single Exposure to Mutagens in Peromyscus and Microtus

Since freshly caught wild mice gave rather uniform MN-PCE counts and since two other rodents, the deermouse (Peromyscus maniculatus) and the meadow vole (Microtus pennsylvanicus), were frequently caught as house mice were being collected from corn cribs, the possibility of also using these as monitors was considered. Towards this end then the deermouse and the meadow vole were compared to two inbred strains, C3H and BALB/c, of the house mouse.

The comparisons involve MN-NCES, MN-PCES and PERCENT PCES in peripheral blood prior to and after treatment with CP (50mg/kg and 200mg/kg), MMC (2mg/kg) and MMS (50mg/kg). The three mutagens were dissolved in saline and injected intraperitoneally.

In Peromyscus the number of MN-PCES, induced by CP, appeared to peak at about 48 hr after treatment (Table 17). This is similar to the pattern observed in the inbred strains. The vole showed only a slight, nonsignificant increase and this only at 24 hr. By 96 hr the MN-PCES had returned to almost the starting levels in both species. The two inbred strains also showed the presence of MN-NCES in peripheral blood whereas the deermouse and the vole showed these to be at or near zero, even after the injection of CP. The

bleeding of mice over 5 consecutive days appeared to stimulate the production of new erythrocytes as indicated by an increase in the percent of PCEs. Earlier studies suggested that CP in the house mouse decreased the release of PCEs into peripheral blood. The percent PCEs observed in mice being bled daily for 5 days but not treated with a mutagen was between 4 and 5. The results obtained for both Peromyscus and Microtus suggested that CP did not inhibit PCE formation in these rodents.

The effects of 200mg/kg CP injected intraperitoneally into BALB/c and Peromyscus are seen in Table 2. Induction of MN-PCEs occurred at a higher rate than with 50mg/kg CP in both groups and there appeared to be a higher survival of MN-NCEs in Peromyscus suggesting that perhaps the removal of MN-NCEs is retarded. Results of experiments to test this hypothesis are given below.

The results for MMC are presented in Table 18. Again the two inbred strains both showed a high production of MN-PCEs. In the house mouse, MMC appeared to be even more effective in the induction of MN than was even the 200mg/kg dose of CP. In the deermouse MMC appeared less effective than CP while in the vole the reverse was seen. In both of these species the increase in MN-PCEs was very slight. Unlike the house mice, neither the deermouse nor the vole, showed many MN-NCEs. Again these cells remained close to zero even after treatment. MMC which affected PCE production in Mus more than CP does not appear to have much effect in Peromyscus or Microtus.

Although MMS, given intraperitoneally, increased MN-PCE levels in both strains of Mus it did not appear to affect Peromyscus at 48 hr. As can be seen in Table 19, there was a problem with this experiment. The deermice showed an uncharacteristically high level of both MN-PCEs and MN-NCEs at the time of injection. There is no obvious explanation for this and this situation was not seen in other experiments in which deermice were used.

This series of experiments indicated that not only MN-PCEs in peripheral blood of house mice but also MN-PCEs in deermice can be used to monitor the environment for recent presence of genotoxic agents. The deermouse may have a narrower range of agents to which it responds as opposed to the house mouse and the response may not be as striking. To determine the validity of this conclusion a much larger battery of test chemicals is required.

Mutagen Exposure and MN Production in Splenectomized Peromyscus and Microtus

In intact Peromyscus, CP increased the MN-PCEs to about 25/1000 PCEs. In splenectomized deermice this jumped to almost 150/1000 PCEs (Table 20). After the peak was reached in both cases there appeared to be a gradual decrease in MN-PCE frequencies. Where in intact Peromyscus the level of MN-NCEs remained extremely low, generally less than 1.0/1000 PCEs with no accumulation, the level in splenectomized mice rose to 45/1000 NCEs with a steady state of around 30/1000 NCEs. These values appear consistent with a 35 day lifespan for NCEs and the injection schedule used. The spleen in Peromyscus appears to be important in reducing MN-NCEs in peripheral blood. Even splenectomized mice that were given only saline had considerably higher frequencies of MN-NCEs than did intact mice given CP.

As in Mus, multiple injections of CP appeared to reduce the percent PCEs in peripheral blood. The effect, however, does not seem as drastic. Also the physiological effect of CP in splenectomized mice was not quite as severe as in the inbreds. Nevertheless by day 70 the mice that remained were in poor condition.

Splenectomy or perhaps splenectomy combined with the bleeding schedule and the handling had an effect on MN-PCEs in peripheral blood. As can be seen from Table 20 an increase in MN-PCEs was observed.

The above results suggest that splenectomy does not enhance the sensitivity of house mice to genotoxins but may in Peromyscus, at least when these animals are treated with CP. It also may permit Peromyscus to be used in chronic studies.

Benzene and Micronucleus Induction in Peromyscus

The long term exposure of house mice to benzene was repeated with the deermouse (Peromyscus maniculatus). The mice were bled seven different times during the exposure schedule. In this experiment because the deermice were more sensitive to CP than the inbreds only 0.5ml of benzene were dropped in the cages. The highest MN-PCE levels detected were reached on day 7 in intact mice and day 4 in both splenectomized and shams animals (Table 21). Beyond day 7, although the animals continued to be exposed to the same amounts of benzene, the MN-PCE counts dropped. The MN-PCE mean values observed in the intact controls may be somewhat higher than they should be because a single animal for no obvious reason gave unusually high counts.

The MN-NCE levels remained very low as expected for Peromyscus with spleens. In the splenectomized mice the MN-NCEs increased as expected based on CP injection experiments. The values approached four but there was a large standard deviation indicating considerable variability. The levels reached by day 11 were within the range expected taking into account the exposure schedule and the lifespan of the NCEs.

This experiment supports the earlier conclusion that splenectomized deermice can be used to monitor chronic exposure to a mutagen even when exposure involves natural routes of intake. There also appeared to be an increased sensitivity in splenectomized mice to benzene at 48 hr, however, the magnitude of the effect is mitigated by the MN-PCE increase observed in both

the sham and intact mice. The high values observed in these groups require further study. Nevertheless, the splenectomized mice appear to retain a higher sensitivity to benzene than did the nonsplenectomized mice.

SUMMARY OF CONCLUSIONS

- 1] The MICRONUCLEUS ASSAY ON PERIPHERAL BLOOD ERYTHROCYTES (MN-PBE assay) in the house mouse, Mus domesticus, was selected as a complementary test to the SISTER CHROMATID EXCHANGE (SCE) ASSAY. Both have been considered as suitable for BIOMONITORING the ENVIRONMENT for changes in GENERAL GENOTOXICITY LEVELS.
- 2] Both acute and chronic exposures to genotoxins can be measured with the MN-PBE assay. Acute exposures result in an increase of micronucleated polychromatic erythrocytes (MN-PCEs) and chronic exposures cause an increase in micronucleated normochromatic erythrocytes (MN-NCEs) in the house mouse.
- 3] A time profile study indicated that there is about a 48 hr lag between exposure and peak levels of MN-PCEs in the blood stream. For maximal sensitivity wild mice must be tested within 48 hr of being brought into the laboratory.
- 4] Multiple exposures to a mutagen caused both an immediate increase in MN-PCEs and a gradual increase in MN-NCEs. The latter occurred at a much slower rate because these cells have a longer lifespan than the PCEs.
- 5] The multiple exposure study placed the lifespan of the MN-NCEs in the house

mouse at about 30 days.

6) Splenectomy had no effect on the frequencies of MN-PCEs, MN-NCEs and total PCEs in peripheral blood of the house mouse.

7) Such factors as sex, age and genetic heterogeneity which could affect the reliability of the MN-PBE assay were found to have no effect in either wild or laboratory mice.

8) The MN-PBE assay was sufficiently sensitive in the house mouse to detect effects of several mutagens dissolved in drinking water and inhaled benzene.

9) Studies of natural populations of mice showed that the MN-PBE test was not as sensitive as the SCE assay. The latter was able to detect seasonal and geographic effects while the former was not. The MN-PBE test does not appear to be suitable for detecting subtle changes in environmental genotoxicity.

10) Also examined were two other rodents common in southwestern Ontario, the deer mouse, Peromyscus maniculatus and the meadow vole, Microtus pennsylvanicus. The nonsplenectomized deer mouse was found useful for acute exposures but not for chronic. The intact meadow vole does not appear suitable for either type of exposure.

11) Splenectomized deer mice appear suitable for both acute and chronic exposures and they respond not only to injected mutagens but also to inhaled benzene. Similar information is not yet available for the meadow vole.

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TABLE 1: Micronucleated cells per 1000 cells in peripheral blood of male C3H mice receiving saline (.5ml/20g body weight), cyclophosphamide (50mg/kg body weight) or mitomycin C (2mg/kg body weight) injections. Four 5-month-old mice were used. The mice were bled at set intervals after the injections to determine the peak effect of the mutagenic agents on the formation of micronuclei.

TIME (hr)	CONTROL			CYCLOPHOSPHAMIDE			MITOMYCIN C		
	MICRONUCLEATED			MICRONUCLEATED			MICRONUCLEATED		
	NCEs	PCEs	PCEs	NCEs	PCEs	PCEs	NCEs	PCEs	PCEs
0	0.78 ±1.06*	1.77 ±0.71	1.22 ±0.63	0.91 ±0.82	1.38 ±1.17	0.86 ±0.52	0.49 ±0.57	0.67 ±0.45	1.40 ±0.37
24	1.94 ±1.56	2.71 ±2.08	2.03 ±0.44	2.07 ±1.21	3.82 ±2.88	1.32 ±0.82	1.33 ±0.96	6.54 ±3.68	1.71 ±0.28
36	1.04 ±1.02	1.56 ±0.87	2.18 ±0.87	2.03 ±1.01	16.51 ±7.13	1.59 ±1.08	0.69 ±0.87	22.07 ±6.13	1.20 ±0.28
48	1.27 ±1.65	1.13 ±1.70	2.60 ±0.92	2.04 ±1.03	42.26 ±12.84	1.19 ±0.73	1.46 ±1.06	55.05 ±9.92	0.76 ±0.36
60	0.21 ±0.43	1.04 ±0.34	3.18 ±1.73	1.85 ±1.09	13.94 ±4.56	1.55 ±0.43	1.52 ±0.97	32.66 ±9.07	0.31 ±0.26
72	1.78 ±0.82	1.88 ±0.53	5.55 ±2.54	1.77 ±0.67	4.31 ±4.34	2.39 ±0.62	2.66 ±1.43	26.58 ±3.16	0.28 ±0.09
96	1.89 ±2.14	3.50 ±1.03	7.47 ±1.64	2.69 ±1.76	5.47 ±4.15	4.54 ±0.90	1.83 ±1.31	7.04 ±2.56	0.73 ±0.26
552	1.14 ±0.33	3.40 ±1.04	0.97 ±0.34	1.91 ±1.61	2.16 ±0.49	1.35 ±0.40	1.85 ±0.39	0.44 ±0.88	1.46 ±0.38

* Standard deviation.

TABLE 2: Effect of a single exposure of cyclophosphamide (200mg/kg) on the frequencies of micronuclei and polychromatic erythrocytes in peripheral blood of two rodent species.

SPECIES BLOOD TAKEN	NO. OF MICE	TIME OF BLEEDING	MICRONUCLEATED		PERCENT PCEs
			NCEs/1000	PCEs/1000	
Mus domesticus (BALB/c)	2 females 2 males	0 hrs	2.38±1.431*	2.10±1.417	1.61±0.644
		48	1.23±1.081	42.88±7.887	0.06±0.121
		96	2.88±1.811	0.00±0.000	0.02±0.043
Peromyscus maniculatus	4 males	0 hrs	0.46±0.531	0.65±0.928	0.79±0.888
		48	1.33±1.780	16.25**	1.33±0.391
		96	0.21±0.422	0.31±0.439	9.19±15.000

* Standard deviation.

** Data available for only one animal.

TABLE 3: Effect of a single exposure of either cyclophosphamide (50mg/kg) or isotonic saline on the frequencies of micronucleated erythrocytes and of polychromatic erythrocytes in peripheral blood of two inbred strains of mice.

TREATMENT AND STRAIN	NO. OF MICE	TIME OF BLEEDING	MICRONUCLEATED		PERCENT PCEs
			NCEs/1000	PCEs/1000	
Saline - intact C3H	4	0 days	0.97±0.346*	0.00±0.000	2.34±0.286
		1	0.77±0.647	2.17±1.997	2.14±0.694
		2	1.11±0.898	1.40±1.244	2.26±0.386
		3	1.98±0.954	2.37±1.859	3.04±0.695
		4	1.08±0.300	1.71±0.589	3.39±0.820
		5	1.63±0.249	0.66±0.810	2.81±1.296
		29	1.51±1.423	2.41±1.712	1.73±0.359
		30	2.60±2.887	1.45±0.574	1.93±1.086
Saline - asplenic C3H	3	0	1.32±0.754	0.92±0.090	1.52±0.595
		1	1.29±0.923	1.66±1.759	2.31±0.764
		2	2.07±0.533	1.88±2.503	3.25±0.467
		3	2.84±2.496	1.15±0.452	3.03±1.047
		4	1.43±1.272	3.09±1.042	2.68±0.446
		5	1.15±0.588	1.53±1.011	3.54±1.691
		29	0.29±0.508	0.94±0.919	2.42±0.897
		30	2.32±1.464	1.19±0.539	2.14±0.095
CP - asplenic C3H	4	0	1.37±1.452	1.14±0.401	2.14±0.827
		1	0.19±0.379	2.55±1.896	1.87±0.446
		2	1.52±1.048	19.47±6.287	2.15±0.723
		3	1.53±0.831	5.16±2.913	2.51±1.393
		4	3.17±2.002	2.47±1.136	4.14±2.206
		5	2.17±1.699	4.84±3.673	5.99±0.879
		29	0.43±0.850	1.88±1.816	2.49±0.428
		30	1.51±1.400	1.92±0.818	2.06±0.559
Saline - intact BALB/c	4	0	3.05±1.584	1.16±0.873	1.75±0.783
		1	1.97±1.0089	2.50±1.135	1.74±0.747
		2	2.43±1.889	0.98±1.385	1.41±0.252
		3	4.07±2.060	2.47±0.492	2.88±0.767
	3	4	1.02±1.097	3.13±2.444	3.32±0.509
		5	2.24±1.572	4.11±1.479	3.40±1.338
		29	2.33±1.071	1.44±0.589	1.37±0.247
		30	1.36±1.206	3.73±2.966	1.66±0.274
CP - asplenic BALB/c	4	0	1.72±0.622	1.58±0.783	1.91±1.096
		1	2.39±1.187	3.78±1.878	1.04±1.058
		2	2.40±1.606	24.89±0.023**	0.83±0.597
		3	3.13±2.093	5.24±2.997	0.74±0.643
		4	2.40±0.727	3.76±1.641	2.28±0.453
		5	5.29±3.363	8.87±2.235	4.04±1.737
		29	3.97±1.525	1.85±1.568	1.89±0.588
		30	2.35±1.058	1.28±1.037	2.02±0.504

* Standard deviation of the mean.

** Data available for only two mice.

TABLE 4: Effect of multiple exposures of either cyclophosphamide (50mg/kg) or isotonic saline on the frequencies of micronucleated erythrocytes and of polychromatic erythrocytes in peripheral blood of intact and splenectomized C3H mice.

DAY OF INJECTION	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs		
		NCEs/1000	PCEs/1000			NCEs/1000	PCEs/1000			NCEs/1000	PCEs/1000			
Cyclophosphamide in splenectomized mice					Cyclophosphamide in intact mice					Saline in splenectomized mice				
0	4	1.83±1.339*	1.34±0.582	2.61±0.998	4	0.71±0.488*	2.22±1.585	2.22±1.205	4	1.21±1.154*	2.29±1.334	2.76±0.950		
3														
7		5.07±1.097	1.83±0.791	2.55±1.197		3.83±2.903	5.35±3.094	2.01±1.160		1.86±1.489	2.49±0.471	4.27±1.035		
10														
15		5.60±1.051	2.13±0.918	1.92±0.902		3.34±1.896	2.02±1.400	5.52±2.744		1.93±0.983	2.32±0.969	1.69±0.498		
17														
19														
21		3.75±2.022	24.60±22.618	2.40±1.383		6.50±1.800	26.39±4.756	3.81±1.870		2.91±0.935	0.96±0.792	2.56±0.383		
23														
25														
28	3	10.95±6.841	13.26±5.837	2.97±2.117	3	7.40±4.805	6.22±3.396	2.83±0.477		3.65±4.097	1.92±2.094	3.34±1.027		
30		7.79±1.588	16.46±7.160	2.30±3.368		12.14±4.047	21.54±10.369	4.83±0.819		1.86±0.975	0.64±0.431	1.00±1.570		
32														
35	2	13.48±1.001	9.83±4.200	1.63±0.637		9.33±0.341	3.42±1.925	4.77±1.152		3.03±1.375	2.92±1.573	1.97±0.780		
37														
39														
42						11.19±2.610	6.61±1.922	4.00±0.691		3.99±0.955	1.95±1.471	5.84±4.933		
44						10.35±0.243	24.24±12.05	4.61±1.088		3.59±2.678	2.90±2.440	5.79±3.194		
46														
49						16.56±9.154	6.92±2.026	6.43±1.174		4.01±0.905	2.85±0.837	3.86±1.903		
51														
53														
56						11.67±6.902	4.24±4.509	4.30±1.731		1.81±1.024	1.59±0.528	3.20±0.809		
58														
60														
63						9.61±5.195	6.01±2.290	3.26±1.354		1.77±1.508	1.18±1.172	3.48±0.931		
65					***				**	1.64±0.881	2.10±0.932	5.03±2.951		
70					3	12.09±4.065	10.01±4.856	2.82±1.304	**	1.43±1.069	0.77±1.534	8.61±6.297		
72									***					
74					**2	10.28±9.001	10.02±9.739	4.09±4.034	***					
77					**1	9.43	2.86	13.66	***					
86					***				**	2.00±1.341	1.68±1.285	2.94±1.172		

* Standard deviation of the mean.

** Sampling only, no injections.

*** No bleeding, no injections.

TABLE 5. Effect of multiple exposures of either cyclophosphamide (50mg/kg) or isotonic saline on the frequencies of micronucleated erythrocytes and of polychromatic erythrocytes in peripheral blood of intact and splenectomized BALB/c mice.

DAY OF INJECTION	NO. OF MICE	MICRONUCLEATED PCER/1000	PERCENT PCER	NO. OF MICE	Cyclophosphamide in intact mice	PERCENT PCER	NO. OF MICE	MICRONUCLEATED PCER/1000	PERCENT PCER	NO. OF MICE	MICRONUCLEATED PCER/1000	PERCENT PCER
Cyclophosphamide in splenectomized mice												
0	4	1.27±0.79*	0.49±0.971	1.86±1.151	4	2.40±1.630*	1.81±1.413	1.67±1.444	4	1.68±0.876*	1.08±0.836	2.31±0.324
3	7	5.05±1.124	3.94±4.278	0.84±0.469		8.32±2.136	1.91±1.119	2.10±0.300		2.92±1.876	2.33±1.397	3.84±0.770
10	15	4.53±5.004	5.43±3.412	2.87±1.322		7.99±5.401	0.58±0.716	2.67±0.683		3.92±1.499	3.18±0.510	3.48±0.242
17	17											
19	19											
21	21	9.00±5.698	38.00±1.892	3.07±1.079		8.66±2.458	40.21±12.141	2.19±0.430		2.22±2.242	2.73±1.241	3.31±0.540
23	23											
25	25											
28	28	16.69±6.307	9.44±2.739	1.27±3.031		10.44±4.731	4.52±1.488	2.28±1.270		2.96±1.444	2.82±2.815	1.33±0.449
30	2	12.97±4.420	37.60±13.703	0.87±0.028		14.50±4.018	35.75±17.011	2.74±0.847		2.02±1.615	2.38±1.239	3.04±1.014
32	0											
35	35											
37	37											
39	39											
42	42											
44	44											
46	46											
49	49											
51	51											
53	53											
56	56											
58	58											
60	60											
63	63											
65	65											
70	70											
72	72											
77	77											
86	86											
Cyclophosphamide in intact mice												
0	4	1.27±0.79*	0.49±0.971	1.86±1.151	4	2.40±1.630*	1.81±1.413	1.67±1.444	4	1.68±0.876*	1.08±0.836	2.31±0.324
3	7	5.05±1.124	3.94±4.278	0.84±0.469		8.32±2.136	1.91±1.119	2.10±0.300		2.92±1.876	2.33±1.397	3.84±0.770
10	15	4.53±5.004	5.43±3.412	2.87±1.322		7.99±5.401	0.58±0.716	2.67±0.683		3.92±1.499	3.18±0.510	3.48±0.242
17	17											
19	19											
21	21	9.00±5.698	38.00±1.892	3.07±1.079		8.66±2.458	40.21±12.141	2.19±0.430		2.22±2.242	2.73±1.241	3.31±0.540
23	23											
25	25											
28	28	16.69±6.307	9.44±2.739	1.27±3.031		10.44±4.731	4.52±1.488	2.28±1.270		2.96±1.444	2.82±2.815	1.33±0.449
30	2	12.97±4.420	37.60±13.703	0.87±0.028		14.50±4.018	35.75±17.011	2.74±0.847		2.02±1.615	2.38±1.239	3.04±1.014
32	0											
35	35											
37	37											
39	39											
42	42											
44	44											
46	46											
49	49											
51	51											
53	53											
56	56											
58	58											
60	60											
63	63											
65	65											
70	70											
72	72											
77	77											
86	86											

* Standard deviation of the mean.

** Sampling only, no injections.

*** No bleeding, no injections.

TABLE 6: Effects of a single bleeding on the induction of micronuclei in polychromatic (PCEs) and normochromatic (NCEs) erythrocytes of peripheral blood in 6 month old BALB/c mice. The amounts of blood taken varied.

AMOUNT OF BLOOD TAKEN	NO. OF MICE	TIME OF BLEEDING	MICRONUCLEATED		PERCENT PCEs
			NCEs/1000	PCEs/1000	
0 ml	6 males	0 hrs	0.87±0.61*	2.60±0.83	2.23±0.77
		72 hrs	1.71±1.41	2.33±1.72	2.47±0.53
0.25 ml	6 males	0 hrs	2.44±1.44	1.60±1.35	1.50±0.50
		72 hrs	1.14±0.77	3.08±0.90	3.87±1.07
0.50 ml	6 males	0 hrs	1.10±1.06	2.19±0.68	1.40±0.49
		72 hrs	1.68±1.63	3.84±1.43	4.10±1.15
	6 females	0 hrs	1.45±1.02	1.37±0.84	1.86±0.55
		72 hrs	1.55±1.39	3.85±1.43	4.10±1.15
	Pooled**	0 hrs	1.27±1.01	1.78±0.85	1.63±0.55
		72 hrs	1.62±1.44	3.84±1.13	4.56±1.06
0.75 ml	6 males	0 hrs	1.38±1.13	2.40±1.84	2.69±2.56
		72 hrs	1.28±1.34	5.35±2.50	6.01±2.08

* Standard deviation.

** A comparison of males and females showed no significant difference when 0.50ml of blood was taken.

TABLE 7: Effects of multiple bleedings on the induction of micronuclei in polychromatic and normochromatic erythrocytes of peripheral blood in 6 month old BALB/c mice. The mice were bled every 24 hours, with 0.5 ml being taken in the first bleeding and 0.06 ml in subsequent bleedings.

TIME OF BLEEDING	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
		NCEs/1000	PCEs/1000	
0 hrs	6	1.85±0.74	2.05±0.67	1.51±0.27
24 hrs	6	1.94±1.29	3.12±0.94	2.69±0.73
48 hrs	6	1.23±1.22	2.78±1.53	4.83±1.08
72 hrs	6	1.86±1.12	6.89±2.89	7.29±2.08
96 hrs	6	1.69±1.27	3.48±1.84	10.95±3.27
264 hrs	6	1.24±0.38	2.59±2.32	2.43±0.78

* Standard deviation.

TABLE 8: Effect of a single exposure of cyclophosphamide (50mg/kg) on the frequencies of micronucleated polychromatic erythrocytes in peripheral blood of male and female mice collected in the summer of 1987.

MICE	NO.	TIME OF BLEEDING AFTER SINGLE INJECTION OF CP		
		0 hr	48 hr	72 hr
1987 females	49	0.90±1.10*	17.00±7.46	4.92±2.83
males	45	0.96±1.17	18.71±8.82	6.18±3.20

* Standard deviation.

TABLE 9: The effect of age in both inbred and wild mice on the induction of micronucleated polychromatic erythrocytes (MN-PCEs) by a single injection of cyclophosphamide (50 mg/kg). The number of N-PCEs per 1000 PCEs is based on 3000 PCEs per mouse.

MUS STRAIN	AGE	NO. OF MICE	MICRONUCLEATED-NCES	
			BEFORE TREATMENT	48 HRS AFTER TREATMENT
C3H	24 months	6	1.83±0.65*	22.49±4.34
C3H	2 months	6	2.18±0.79	25.94±5.63
BALB/c	4 months	6	2.10±1.00	29.65±10.48
wild	24 months	6	1.44±0.86	24.33±10.56
wild	12 months	6	2.18±1.01	28.39±4.50
wild	2 months	6	1.59±0.95	25.16±5.16

* Standard deviation.

TABLE 10: Effect of a single exposure of cyclophosphamide (50mg/kg) on the frequencies of micronucleated polychromatic erythrocytes in peripheral blood of adult and juvenile mice collected in the summer of 1987, and of mice collected in the summer of 1986 (more than 14 months old at testing) and mice collected during the summer of 1987 (less than five months old).

MICE	NO.	TIME OF BLEEDING AFTER SINGLE INJECTION OF CP		
		0 hr	48 hr	72 hr
1987 juveniles*	53	0.96±1.04**	18.69±9.37	5.81±3.21
adults	41	0.93±1.27	16.46±6.04	4.92±2.63
pooled	94	0.95±1.14	17.82±8.14	5.52±3.06
1986 pooled	24	1.13±1.19	19.67±9.60	5.52±3.06

* Mice were classified as juveniles if they weighed less than 12 gm.

** Standard deviation.

TABLE 11: Effect of a single exposure of cyclophosphamide (50mg/kg) on the frequencies of micronucleated polychromatic erythrocytes in peripheral blood of an inbred strain of mice and wildcaught mice collected in two summers. The 1986 mice were at least 15 months old when tested and the 1987 mice were probably between 2 and 5 months of age.

MICE	OF MICE	TIME OF BLEEDING AFTER SINGLE INJECTION OF CP		
		0 hr	48 hr	72 hr
Inbred strain:				
BALB/c	15	1.60±1.82*	28.60±7.40	9.20±3.70
Wild 1986:				
Essex south	4	0.50±1.00	19.75±8.26	3.25±2.63
Essex west	5	1.20±1.30	28.40±11.55	4.80±3.96
Tilbury north	6	1.50±1.60	18.33±8.60	3.50±1.90
Blenheim south	4	1.25±0.96	21.00±6.98	5.50±1.00
West Lorne south	5	1.00±1.02	13.40±5.41	4.05±5.15
Wild 1987:				
Amherstburg	4	0	29.50±5.45	8.25±3.59
Essex south	20	1.35±1.04	20.10±6.87	6.05±3.28
MacKay's corners	20	0.75±0.91	12.65±6.12	4.00±2.49
Ridgetown east	19	1.11±1.56	17.37±7.83	4.68±2.91
Rodney west	15	0.27±0.59	17.80±9.13	7.33±2.77
West Lorne east	8	1.63±1.19	15.63±4.63	5.75±1.49
Fingal west	8	0.88±0.83	22.50±9.56	5.00±3.55

* Standard deviation.

TABLE 12: Induction of micronuclei in peripheral blood and sister chromatid exchanges in bone marrow cells of either C3H or BALB/c mice by exposure to methyl methanesulfonate or cyclophosphamide in drinking water for a 15 day period.

MUTAGEN AND DOSE	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs	SCEs +sem
		NCEs/1000	PCEs/1000		
Methyl methanesulfonate:					
240mg/100ml	1 BALB	1.7400	4.5000	0.6000	6.90 ±2.15
60mg/100ml	5 BALB	1.2960 ±0.7190*	5.0140 ±1.1450	1.0420 ±0.3157	6.42 ±0.48
60mg/100ml	5 C3H	1.5660 ±0.5300	6.3620 ±2.5861	1.3540 ±0.5932	6.41 ±1.10
15mg/100ml	5 C3H	1.6760 ±1.6764	1.5420 ±1.0944	2.0020 ±1.2051	4.94 ±0.81
Cyclophosphamide:					
236mg/100ml	3 BALB	3.4200 ±0.7110	23.6133 ±13.5806	0.9966 ±0.1921	21.67 ±11.79
118mg/100ml	5 BALB	3.3820 ±1.5213	28.4020 ±13.9972	1.1180 ±1.1180	10.24 ±2.21
Controls:					
tap water	5 C3H	1.1060 ±0.9095	0.9120 ±1.1314	1.3460 ±0.2514	4.43 ±0.71
tap water	5 Balb	1.3500 ±1.1729	2.5640 ±0.7495	1.1680 ±0.2401	
sugar water	5 Balb	1.0300 ±1.1729	1.9060 ±0.7495	1.1680 ±0.2401	4.83 ±0.35

* Standard deviation.

TABLE 13: Induction of micronuclei in polychromatic erythrocytes (PCEs) and normochromatic erythrocytes (NCEs) by exposure of mice on two consecutive days to benzene vapours. Each day benzene was dropped hourly beginning at 10:00 a.m. and ending at 4:00 p.m. into a corner of the cage. BALB/c male mice were used. Some had been splenectomized.

MOUSE CONDITION	NO. OF MICE	BENZENE TREATMENT (ml/hr)	MN-NCEs/1000	MN-PCEs/1000	PER CENT PCEs
Intact	5	0	2.12±1.33*	3.05±1.05	2.58±0.45
	6	0.25	2.28±1.84	3.90±1.96	1.78±0.40
	5	0.50	2.38±1.51	11.36±3.17	1.90±0.66
Sham	3	0.25	0.88±0.88	4.65±1.46	3.75±1.29
Splenectomized	6	0	1.83±1.23	4.40±3.02	2.41±1.11
	6	0.25	1.73±0.78	5.26±1.90	2.09±0.47

* Standard deviation.

TABLE 14: Induction of micronuclei in peripheral blood of male BALB/c mice by exposing the mice hourly to 1 ml of benzene, 7 times per day beginning at 10:00 a.m. and ending at 4:00 p.m. for 16 days.

EXPOSURE TIME	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
		NCEs	PCEs	
0 hr	6	2.62±1.19*	2.00±1.01	1.28±0.96
48 hr	6	2.33±1.53	34.13±14.00	0.62±0.53
96 hr	5	3.09±1.18	52.34±16.04	0.43±0.24
168 hr	4	6.13±3.17	54.80±23.77	1.47±0.53
264 hr	3	7.69±3.25	29.22±8.10	1.02±0.63
336 hr	3	14.95±3.97	11.81±1.69	4.11±0.48
384 hr (last expos.)	3	10.29±3.76	28.57±11.52	4.52±1.50
480 hr	3	12.24±2.02	4.83±3.16	8.45±1.67

* Standard deviation.

TABLE 15: Frequencies of micronucleated polychromatic and normochromatic erythrocytes in peripheral blood obtained from the suborbital sinus of mice caught in 1986. The last column is a measure of the formation of new erythrocytes.

LOCATION	NO.	DATE OF CAPTURE	MEAN MN-PCE PER 1000PCE	MEAN MN-NCE PER 1000NCE	MEAN PERCENT PCE PER TOTAL
<u>Essex County</u>					
McKim east	18	4/18/86	1.00±1.174*	0.73±0.770	2.71±1.871
McKim west	17	4/25/86	1.69±1.376	0.77±0.553	4.08±2.328
Renaud north	20	5/28/86	0.63±0.784	0.95±0.778	2.71±3.523
Renaud middle	13	5/28/86	2.19±2.404	0.27±0.665	2.14±1.523
Amlin	16	6/6/86	1.89±1.401	0.90±0.766	1.69±1.083
Goolan north	5	6/12/86	0.73±0.732	0.54±0.787	0.54±0.439
Goolan south	7	6/12/86	0.95±1.114	0.93±0.794	1.06±0.637
Holden	8	6/13/86	1.48±1.057	1.09±0.580	1.72±0.795
C. Wilkinson	9	6/26/86	1.38±0.500	1.57±1.153	1.91±1.046
Farrough	20	8/6/86	1.56±1.344	0.99±1.059	2.22±0.967
Boide	24	9/5/86	0.96±0.991	0.67±1.102	1.42±0.927
<u>Kent County</u>					
Dilliot	4	5/9/86	0.68±0.844	1.13±1.229	2.17±2.064
Lucio	28	5/23/86	2.72±1.220	0.57±0.814	3.67±2.518
Sheldon	5	5/23/86	1.53±1.494	1.65±2.956	1.50±1.081
Whittington	3	6/9/86	0.90±0.926	0.95±1.125	2.59±1.761
<u>Elgin County</u>					
Oskar	16	6/20/86	0.77±0.758	1.73±1.552	3.63±5.829
Virog	1	6/26/86	3.92	1.45	1.01
<u>Controls</u>					
C3HeB/FeJ	3	5/9/86	2.33±0.586	1.63±0.26	1.59±0.659
	4	5/22/86	1.55±2.055	1.12±0.925	1.83±0.348
	3	5/28/86	2.10±1.489	1.39±1.660	2.68±2.130
	4	6/6/86	2.79±2.500	1.01±0.900	1.51±0.304
	4	6/12/86	2.43±2.094	0.85±0.102	1.22±0.317
	4	6/25/86	1.83±0.794	0.85±0.670	2.39±0.447
	4	6/26/86	0.69±0.863	1.14±0.591	1.80±0.464

* Standard deviation.

TABLE 16: SCE levels in wild male mice collected from corn cribs in three regions of southwestern Ontario before, during and after the spraying of crops with herbicides over a four year period. Mice collected in 1984 through 1986 had 50 mg BrdU tablets implanted for SCE staining whereas the 1983 were injected with 80 mg of BrdU.

YEAR	LOCALITY	SCE COUNTS + S.E.M.		
		PRESPRAYING	SPRAYING	POST-SPRAYING
1986	Essex County	4.64±0.22 (20)	6.76±0.16 (34)	6.01±0.24 (32)
	Kent County	5.69±0.41 (27)	5.86±0.38 (17)	
1985	Essex County	5.16±0.16 (30)	7.07±0.43 (11)	7.21±0.84 (10)
	Kent County		5.92±0.36 (37)	
	Elgin County		4.74±0.31 (7)	
1984	Essex County	5.70±0.19 (28)	6.35±0.17 (32)	
	Kent County	4.65±0.43 (19)	6.66±0.24 (38)	4.89±0.18 (30)
	Elgin County		6.62±0.46 (20)	
1983	Pooled data	5.99±0.32 (12)	9.22±0.86 (10)	

The numbers in parentheses are the sample sizes.

TABLE 17: Effect of a single exposure of cyclophosphamide (50mg/kg) on the frequencies of micronuclei and polychromatic erythrocytes in peripheral blood of three rodents.

SPECIES BLOOD TAKEN	NO. OF MICE	TIME OF BLEEDING	MICRONUCLEATED		PERCENT PCEs
			NCEs/1000	PCEs/1000	
<i>Mus domesticus</i> (C3H)	2 females	0 hrs	0.96±1.361*	1.45±2.048	1.46±0.218
		24	0.00±0.000	1.73±1.057	1.64±0.340
		48	0.73±1.035	20.34±0.397	1.79±0.110
		72	1.20±0.748	6.05±1.916	2.63±1.117
		96	1.81±0.017	0.87±1.235	6.49±3.576
<i>Mus domesticus</i> (BALB/c)	2 males	0 hrs	1.91±1.488	0.92±1.299	1.32±1.218
		24	2.67±1.000	3.42±3.531	1.93±1.217
		48	2.66±1.062	32.98±0.355	1.46±0.207
		72	2.81±1.718	8.63±0.967	1.47±0.816
		96	2.96±0.505	2.96±1.469	5.09±0.359
<i>Peromyscus</i> <i>maniculatus</i>	4 males	0hrs	0.00±0.000	0.24±0.487	1.23±0.524
		24	0.00±0.000	3.09±3.821	1.18±0.790
		48	0.00±0.000	11.64±11.276	0.28±0.324
		72	0.00±0.000	1.62±1.487	5.11±5.717
		96	0.00±0.000	1.05±1.626	10.50±13.488
<i>Microtus</i> <i>pennsylvanicus</i>	4 males	0 hrs	0.16±0.315	0.00±0.000	1.26±0.322
		24	0.00±0.000	2.18±3.807	1.13±0.866
		48	0.00±0.000	0.50±0.993	1.54±1.316
		72	0.00±0.000	1.31±0.752	3.28±1.426
		96	0.00±0.000	1.04±1.547	5.66±1.901

* Standard deviation.

** A comparison of males and females showed no significant differences in any of the groups.

TABLE 18: Effect of a single exposure of mitomycin C (2mg/kg) on the frequencies of micronuclei and polychromatic erythrocytes in peripheral blood of three rodent species.

SPECIES BLOOD TAKEN	NO. OF MICE	TIME OF BLEEDING	MICRONUCLEATED		PERCENT PCEs
			NCEs/1000	PCEs/1000	
Mus domesticus (C3H)	2 females	0 hrs	0.00*	0.97	1.29
		24	3.67	0.94	0.09
		48	0.58±0.746**	32.00	0.15
		72	2.87	0.00	0.00
		96	1.69	2.69	0.00
Mus domesticus (BALB/c)	2 males	0 hrs	0.84±0.137	1.95±1.354	2.55±0.129
		24	1.53±0.942	12.28±2.154	2.37±0.959
		48	2.24±0.278	80.29±0.028	0.75±0.195
		72	2.18±1.670	6.89	0.09±0.011
		96	4.57±3.977	11.01±2.054	0.34±0.267
Peromyscus maniculatus	4 males	0 hrs	0.00±0.000	2.32±0.630	1.59±0.675
		24	0.00±0.000	3.95±4.293	1.30±0.674
		48	0.00±0.000	3.89±1.289	1.60±1.643
		72	0.30±0.417	1.63±0.999	5.16±4.195
		96	0.00±0.000	1.92±2.712	11.75±10.710
Microtus pennsylvanicus	4 males	0 hrs	0.00±0.000	0.00±0.000	0.17±0.246
		24	0.00±0.000	0.94±1.334	0.40±0.563
		48	0.00±0.000	2.44±0.637	1.08±1.364
		72	0.00±0.000	1.46±0.707	1.43±0.548
		96	0.00±0.000	1.97±2.484	9.65±5.680

* Data available for only one animal when no standard deviation is given.

** Standard deviation.

TABLE 19: Effect of a single exposure of methyl methanesulfonate (50mg/kg) on the frequencies of micronuclei and polychromatic erythrocytes in peripheral blood of two rodent species.

SPECIES BLOOD TAKEN	NO. OF MICE	TIME OF BLEEDING	MICRONUCLEATED		PERCENT PCEs
			NCEs/1000	PCEs/1000	
Mus domesticus (C3H)	4 males	0 hrs	0.96±0.690*	0.69±0.458	1.64±0.421
		48	2.37±2.217	9.62±1.397	2.93±0.790
Mus domesticus (BALB/c)	4 males	0 hrs	2.00±1.458	2.89±0.791	1.49±0.425
		48	2.11±1.752	4.45±4.107	4.07±2.645
Peromyscus maniculatus	2 females	0 hrs	7.50±5.194	4.45±4.107	4.67±2.645
	2 males	48	0.00±0.000	1.30±1.841**	0.73±1.449
Mus domesticus (C3H) ***	4 males	0 hrs	2.41±1.541	1.90±2.065	2.62±0.541
		48	1.85±0.871	1.88±2.289	3.16±1.352

* Standard deviation.

** Lack of sufficient PCEs in 2 mice.

*** Control group receiving only an isotonic saline injection.

TABLE 20. Effect of multiple exposures of either cyclophosphamide (50mg/kg) or isotonic saline on the frequencies of micronucleated erythrocytes and of polychromatic erythrocytes in peripheral blood of intact and splenectomized P. maniculatus.

DAY OF INJECTION	NO. OF MICE	PERCENT PCES	MICRONUCLEATED PCES/1000	NO. OF MICE	PERCENT PCES	MICRONUCLEATED PCES/1000	NO. OF MICE	PERCENT PCES	MICRONUCLEATED PCES/1000	PERCENT PCES			
Cyclophosphamide in splenectomized mice													
0	4	0.62±0.782*	2.43±2.317	2.43±1.426	4	0.00±0.000*	0.85±1.227	1.72±1.097	3	0.00±0.000*	2.40±1.352	4.76±0.080	
3													
7													
10		2.16±0.641	5.37±1.842	3.17±0.986		0.00±0.000	0.00±0.000	3.42±1.067		3.62±1.282	2.77±1.117	2.15±0.502	
15		10.15±5.949	9.53±4.228	5.69±1.889		0.63±1.256	1.25±1.359	3.68±1.623		5.75±3.531	5.38±6.943	14.77±20.740	
17													
19													
21		15.05±4.896	148.08±51.266	1.98±1.997		0.17±0.348	21.76±16.124	1.76±0.875		3.55±0.855	5.99±3.541	8.80±9.417	
23													
25													
28		19.77±9.100	17.17±4.900	1.39±2.209		0.00±0.000	3.93±3.325	2.75±1.872		2.44±2.527	4.08±4.907	5.55±2.664	
30		16.21±5.104	126.79±57.283	3.85±1.162		1.17±0.746	24.98±19.352	3.12±1.152		0.62±1.067	5.71±7.336	7.45±1.853	
32													
35	3	31.48±7.344	23.89±15.216	3.58±2.148		0.24±0.485	1.86±1.096*	3.24±0.977					
37													
39													
42		33.54±9.685	17.21±2.755	3.87±1.520		0.00±0.000	1.93±0.842	1.14±1.490		4.81±3.603	6.90±6.598	8.77±8.104	
44	2	30.74±0.807	96.25±55.094	2.60±1.467		0.17±0.332	17.20±7.157	3.36±1.215		6.05±6.492	6.86±4.715	13.22±16.656	
46													
49		45.11±9.314	14.81±2.665	3.80±2.555		0.20±0.392	4.09±1.963	6.19±1.598		3.40±3.734	3.48±2.231	9.30±8.512	
51													
53													
56		37.60±4.107	7.66±5.429	3.55±0.483		0.19±0.389	4.62±2.051	3.74±1.675		2.69±2.378	4.19±3.310	5.16±0.915	
58													
60													
63	1	57.03	16.29	9.00	3	0.00±0.000	2.15±2.014	4.68±2.696		1.36±0.984	3.84±1.727	3.77±1.784	
65	**	65.52	55.36	9.38	***					**	1.70±1.492	4.50±2.265	6.70±1.231
70	**	29.05	18.69	15.32	***	1.59±2.337	1.56±1.992	3.00±1.305		**	4.72±4.854	6.23±7.936	14.41±8.824
72	***				***					***			
77	***				**	0.47±0.409	0.53±0.464	5.30±2.361		***			
86	**	2.04	1.96	1.21	***					**	1.48±0.809	2.02±1.246	1.58±0.972

* Standard deviation of the mean.

** Sampling only, no injections.

*** No bleeding, no injections.

TABLE 21: Induction of micronuclei in peripheral blood of deermice, *Peromyscus maniculatus*, by exposing the mice hourly to 0.5ml of benzene vapour, 7 times per day beginning at 10:00 a.m. and ending at 4:00 p.m. for 16 days.

MOUSE CONDITION	BENZENE EXPOSURE	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
			NCEs	PCEs	
Intact	0 days	5	0.15±0.344	1.24±0.775	1.32±0.335
	2	5	0	3.58±5.949	2.27±1.637
	4	5	0	7.10±8.619	5.82±2.523
	7	4	0.26±0.525	9.85±8.667	7.52±4.033
	11	4	0	7.86±13.890	4.80±0.921
	17	4	0	1.45±0.739	3.37±1.255
	35	4	0	0.68±0.866	2.02±0.749
Sham	0	5	0	1.65±1.524	1.09±0.491
	2	5	0	6.07±3.449	1.99±0.653
	4	5	0	6.78±3.00	2.83±1.564
	7	5	0	2.75±2.121	5.59±2.956
	11	5	0.45±0.411	2.57±1.607	2.71±0.742
	17	5	0	3.08±2.360	3.59±0.991
	35	5	0	0.73±0.410	1.60±0.628
Splenectomized	0	5	1.90±1.082	3.49±1.790	1.42±0.970
	2	5	2.47±1.609	9.40±3.554	2.06±1.448
	4	5	1.75±1.228	14.84±7.965	3.35±1.067
	7	5	2.61±2.323	10.78±6.885	5.33±1.560
	11	4	3.50±1.828	8.59±6.452	3.73±1.747
	17	4	4.40±3.444	6.67±2.386	4.60±2.298
	35	4	3.68±3.867	4.40±.994	2.31±1.682

* Standard deviation.

UTILIZATION OF ESTABLISHED AIR
POLLUTION MONITORING NETWORKS
IN ONTARIO FOLLOWING NUCLEAR INCIDENTS

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Abstract

This paper describes the initial phases of a study established to investigate the potential of using conventional air pollution monitoring networks for monitoring of radioactive iodine fission products following nuclear incidents. The work is being carried out by Atomic Energy of Canada Limited at the Chalk River Nuclear Laboratories and is funded by the Ontario Ministry of the Environment. Supplies of charcoal-loaded filter paper have been identified and five types have been selected for evaluation. The filter media are being evaluated for both methyl iodide and molecular iodine removal efficiency under varying conditions of relative humidity, challenge gas face velocity, and adsorbate concentrations. Recommendations on an approach to implementing a monitoring program utilizing this form of sampling media will be presented at the study's conclusion, should final results prove positive.

1. INTRODUCTION

Significant benefits can be obtained by monitoring airborne radionuclides within existing air pollution monitoring networks following nuclear incidents. This study investigates the potential of using charcoal-loaded filter paper to monitor radiologically significant iodine fission products with currently installed equipment used for routine monitoring of air pollutants.

Environmental monitoring is a key element in identifying the extent and consequences of releases of radioactive materials to the atmosphere during and immediately following nuclear incidents. As a consequence, nuclear utilities include substantial provisions for deploying both personnel and equipment to monitor airborne radioactivity in their emergency plans. In regions remote from the scene of an incident, where government agencies assume the responsibility of monitoring, logistical problems may be encountered in deploying monitoring equipment. Similar problems can be encountered with monitoring plumes of a transboundary origin. Many difficulties could be overcome if existing air pollution monitoring networks utilizing high volume air sampling equipment could be simply and effectively adapted to collect airborne radionuclides.

For particulate radioactive contaminants, particulate filters already used in high volume air sampling networks would be an effective sample media. However, this media has no ability to trap gaseous radiiodines. Experience in the nuclear industry, and following the accidents at Three Mile Island and Chernobyl, demonstrate radioactive iodines are predominantly in the gaseous state. As they are probably the most radiobiologically significant fission products, an effective monitoring program following a nuclear incident must have the ability to collect radiiodines, the most notable of which is I-131. Several approaches are available to accomplish this. One method would be to deploy expensive portable high volume samplers using special deep bed charcoal canisters. Another would be to design and manufacture carbon deep bed filters which could be installed on the high volume air sampler. A third method, which does not require additional equipment purchase or modifications would be the use of charcoal-loaded filter paper. Although likely to have a lower collection efficiency for radiiodines, particularly organic iodides, charcoal-loaded filter papers would be the easiest to deploy at a much lower cost.

The focus of this study is to examine the usefulness of charcoal-loaded filter papers for iodine monitoring by determining their iodine retention efficiency. The specific objectives are:

- to identify sources of charcoal-loaded filter media and to select those most suitable for environmental monitoring of radiiodines;
- to test, under controlled laboratory conditions, the collection efficiency of up to 5 different filter media; and
- to review the potential of using the media in high volume air samplers such as those used in conventional air pollution measurements.

2. CHARCOAL-LOADED FILTER MEDIA SELECTION

At present, four suppliers of charcoal-loaded filter paper have been identified. From these suppliers five filter types have been identified as potentially suitable for radiiodine collection. The suppliers and media types are listed in Table 1.

Table 1
Charcoal-Loaded Filter Paper Suppliers

<u>Supplier</u>	<u>Address</u>	<u>Media</u>
Dexter Materials Division	Burlington, Ontario	Grade 1283
"	"	Grade 4703
F&J Specialty Products	Miami Springs, Florida	CI 47
Whatman Paper Division	Clifton, New Jersey	Grade 72
Extraction Systems Inc.	Norwood, Mass.	Hyper Series 6-2

The factors considered in selecting potential sample media included: the carbon loading of the media (g/m^2); the physical stability and durability of the charcoal/fibre matrix (some grades tend to be quite friable); and the addition of chemicals (KI, Triethylenediamine) which would enhance the collection efficiency for radiiodines, particularly organic iodides. The physical properties of the media selected to date are shown in Table 2.

Table 2
Filter Media Physical Properties

<u>Media</u>	<u>Adsorbent Type</u>	<u>Carbon Loading (g/m^2)</u>	<u>Chemical Impregnant</u>
Dexter Grade 1283	Activated Carbon	117	---
Dexter Grade 4703	Activated Carbon	80	---
F&J CI 47	Activated Carbon	n/a*	---
Whatman Grade 72	Activated Carbon	195	---
Extraction Sys.	Activated Carbon	440	Triethylenediamine
Hyper Series 6-2			

* n/a - not available

3. EXPERIMENTAL DESIGN

3.1 Test Conditions

Representative samples (approximately 50 mm diameter discs) of the charcoal-loaded filter media are tested for both molecular iodine (I_2) and methyl iodide (CH_3I) removal efficiency under controlled laboratory conditions. Environmental parameters being varied in the study, which may effect removal efficiency, are adsorbate concentration, challenge gas face velocity, and relative humidity. The test parameters and their values are summarized in Table 3.

Table 3
Test Conditions

<u>Parameter</u>	<u>Value</u>
Temperature (°C)	25
Adsorbate Concentration (mg/m ³)-CH ₃ I	0.01, 0.1
-I ₂	0.01, 0.1
Relative Humidity (%)	40, 75, 95
Face Velocity (cm/s)	35, 50, 60

The adsorbate concentrations of 0.01, and 0.1 mg/m³ for both I₂ and CH₃I correspond to I-131 activity concentrations of approximately 1 μ Ci/m³ and 10 μ Ci/m³ respectively. These levels are likely several orders of magnitude greater than those which could be expected following a major nuclear incident. This, of course, would depend primarily on the distance from the nuclear incident and the sampling location. For instance, following the Chernobyl accident, maximum I-131 concentrations in Poland and Scandinavian countries ranged from 3×10^{-5} μ Ci/m³ to 1.6×10^{-2} μ Ci/m³, while concentrations downwind in the U.S.S.R. ranged from 8.5×10^{-1} μ Ci/m³ (10 miles) to 6.1×10^{-4} μ Ci/m³ (1,250 miles) [1]. The iodine-in-air concentrations used in the study are, therefore, believed to be significantly higher than those which would be observed during environmental air sampling following a nuclear incident. However, use of these concentrations will result in iodine loadings approaching the generally accepted maximum loading ranges of 1-10 mg/g of charcoal.

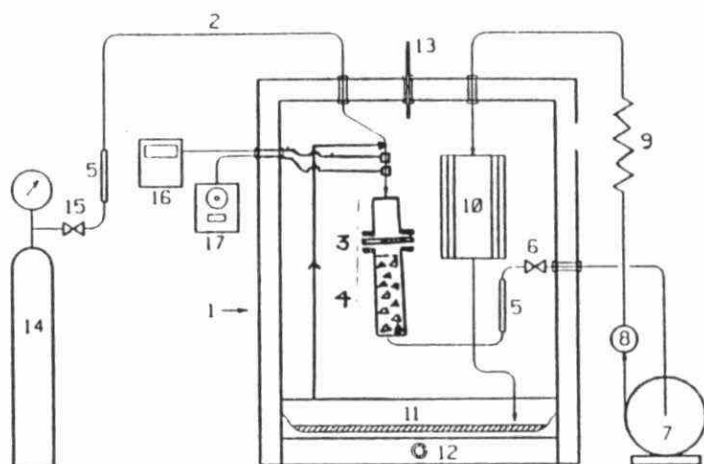
The face velocities of 35, 50 and 60 cm/s match those experienced by a high volume air sampler operating at 40-60 cfm with a 20 cm x 25 cm filter.

3.2 Test Equipment

A functional diagram of the test equipment is shown in Figure 1. The system is composed of the following functional components:

- environmental chamber with temperature control;
- constant humidity control;
- adsorbate (CH₃I and I₂) gas generator and injection line;
- charcoal-loaded proper test column;
- challenge gas recirculation line;
- NaI gamma spectroscopy analysis system; and
- computing unit.

The range and accuracy of the test parameters, and their control and monitoring by the test equipment is shown in Table 4.



- | | |
|---------------------------------|--|
| 1. Environmental Test Chamber | 10. Heat Exchanger |
| 2. Injection Line | 11. Sulphuric Acid Bath |
| 3. Charcoal-Loaded Filter Paper | 12. Temperature Controller |
| 4. Back-up Charcoal | 13. Thermometer |
| 5. Flowmeter | 14. Cl_2 Challenge Cylinder |
| 6. Flow Control Valve | 15. Cl_2 Feed Control Valve |
| 7. Oil-Less Air Pump | 16. Cole Parmer Digital Hygrometer |
| 8. Line Filter | 17. Honeywell Relative Humidity Readout Instrument |
| 9. Air-Cooled Discharge Line | |

Figure 1
Test Equipment Functional Diagram

Table 4
Technical Specifications of Test Equipment

	Temp.(°C)	RH (%)	Test Flow (L.min ⁻¹)*
Control Range	25-65	40-98	15-50
Monitoring Range	0-100	0-100	2-50
Control of System Parameters	± 0.5	± 2.0	± 1.0
Monitoring of System Parameters	± 0.25	± 1.0	± 0.75

* Standard Pressure

4. FUTURE WORK

The actual experimental work in this project, at the time of writing this report, is at a very preliminary stage and results are thus not yet available. The future work will, therefore, consist first of completing the testing program. Results will then be analyzed and the potential determined for using one or more of the charcoal-loaded filter papers studied for environmental radio-iodine monitoring.

The primary acceptance criteria for the filter media, will be based on the Protective Action Levels (PALs) outlined in the Province of Ontario Nuclear Emergency Plan [2]. It is felt the removal efficiencies must be high enough to allow detection of iodine-131 in air concentrations which would result in the Lower Level PAL (Thyroid) for sheltering, assuming a 24 hour sampling period. This value is 0.3 rem - Thyroid. At or above this level, the appropriate protective measures should be applied unless valid reasons exist for deferring actions.

The use of charcoal-loaded filter papers as a media for environmental monitoring for radiolodines at post accident concentrations is believed feasible. Some studies performed in the early 1960's in the United Kingdom [3,4], indicated quite high removal efficiencies I_2 (>90%) but relatively low efficiencies for organic species such as CH_3I (~5-10%). There are, however, some indications that recent filter media have a higher efficiency for organic iodides. A Japanese study [5] indicates removal efficiencies with and without triethylenediamine impregnant greater than 95% and 80%, respectively, for a gas stream containing 60% inorganic and 40% organic iodide.

5. REFERENCES

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INTRODUCTION

Landfills are the most common means of disposing of municipal garbage or refuse. In a landfill operation, the wastes are regularly covered with earth to control windblown litter and to discourage or eliminate the nuisance of rodents and scavenger birds. The decomposition of the refuse produces a number of gases, some of which may have very offensive odours. The purpose of this paper is to describe the design, construction and testing of a system to dispose of these gases at a major Metropolitan Toronto landfill.

Before discussing the system it is perhaps useful to review, in simple terms, the process of decomposition and gas production within a landfill. The decomposition of landfilled refuse occurs by both aerobic and anaerobic degradation of the organic matter. Oxygen is normally entrapped during the initial placement of refuse in the landfill. Aerobic micro-organisms decompose the organic wastes, consuming the available oxygen and producing mainly carbon dioxide and water. This process also generates heat, and elevated temperatures may occur within the landfill.

When the available oxygen is depleted, anaerobic micro-organisms become dominant, and the decomposition process becomes an anaerobic process. This switch-over, from aerobic to anaerobic, usually occurs within a few weeks of the refuse placement in the landfill. The major products of the anaerobic decomposition are methane and carbon dioxide. The proportion of methane to carbon dioxide will depend on the type of waste. Typically, a municipal landfill gas will have a methane content of 50 to 55 percent and a carbon dioxide content of 45 to 50 percent. It must be appreciated that these are typical values, and the considerable variation occurs in practice and has been recorded in various technical writings.

The total yield of gas is dependent on the chemical characteristics of the refuse. Theoretically, a "typical" municipal waste may produce a total of about 268 L gas/Kg of wet refuse. Landfill studies indicate that actual

gas production is much lower, approximately 120 L gas/Kg of wet refuse. This production is over a long period of time, exceeding 20 years after refuse placement.

Associated with the decomposition of organic wastes is the production of trace amounts of organic gases, such as thiols (mercaptans) which have a pronounced offensive odour. Thiols are formed by the replacement of a hydrogen atom by an aliphatic, aromatic or hetero-cyclic radical forming a sulphhydryl group. An example of a simple thiol is ethanethiol, which is a component of skunk fluid.

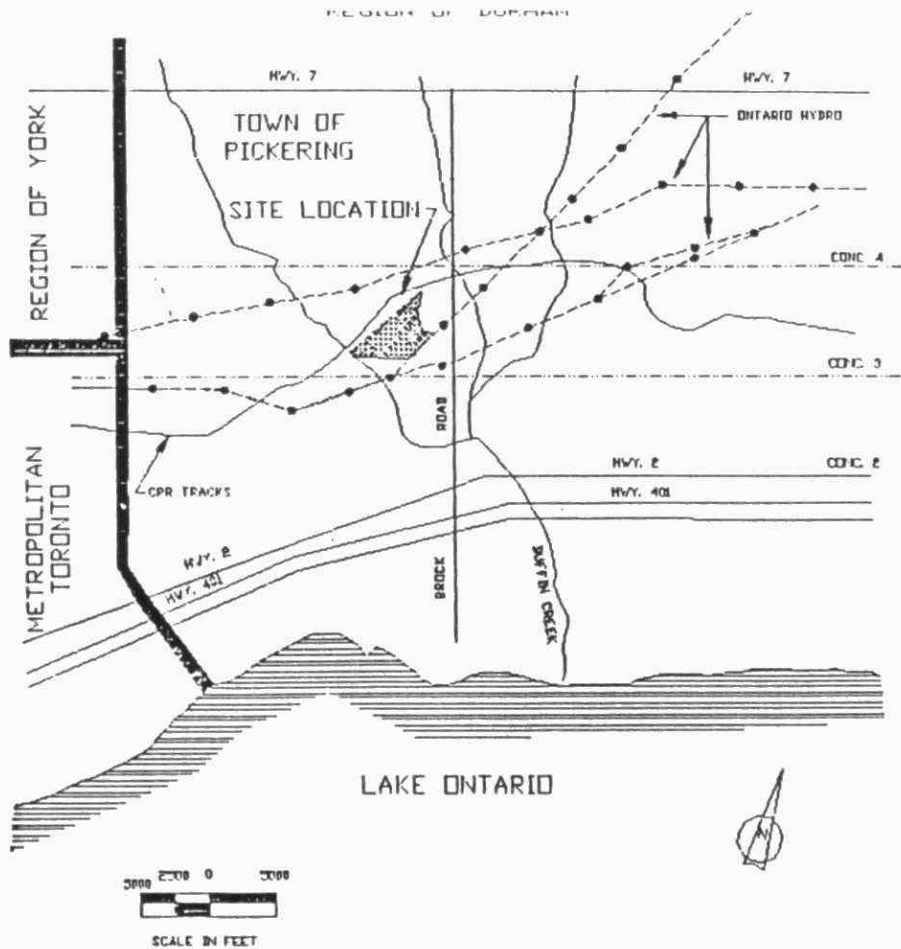
The odour of thiols can be detected by the human nose in concentrations as low as 20 parts per trillion. Like hydrogen sulfide, from which they are derived, thiols are toxic; however, concentrations in the air around a landfill are generally more of a nuisance than a health hazard. Because of the vast array of synthetic compounds which find their way to landfills, there are many other trace organics some of which are toxic, contained in landfill gas. Some recent studies at the Waste Research Unit of the Harwell Laboratory in Oxford, U.K., as reported by Young and Hessman at the GRCDA 1985 Conference in San Antonio, identified 116 different trace compounds in landfill gases sampled at three landfill sites. The total trace gas levels were between 0.07 and 0.29 percent by weight of the gas.

These trace organic gases can, in general, be destroyed by incineration. Hence, one means of controlling the odour emanating from a landfill is to collect and incinerate the gas. The high methane content makes landfill gas combustible and the incineration is self supporting. This is the basic concept of the _____ system that is the subject of this paper.

THE SITE

The Brock West Landfill Site is owned by Metropolitan Toronto and is operated by the Works Department. This site is located in the Town of Pickering, about ten kilometres east of the Metropolitan Toronto boundary. The site contains 121.4 hectares, of which 80.9 will be used for landfill. The location of the site is shown on Figures 1.

REGION OF PICKERING



LOCATION MAP

FIGURE No. 1

The site was first opened in 1973 and has a planned total capacity of 11,342,000 cubic meters of refuse. The site is partly underlain by sand and partly by clay. Where the landfill is on sand, a bentonite-sand liner has been installed to control leachate escape to the ground water. The ground water below the liner is controlled by a major underdrain which originally discharged to a local stream and presently connected to the sanitary sewer system. Leachate is collected in drains above the liner and is discharged into the local sanitary sewer.

As the site developed, including major residential development closer to the landfill site, complaints of objectionable odours were increasing at an alarming rate. Generally the complaints coincided with certain climatic conditions when wind and inversions would keep the gas plume close to the ground and carry it in to the residential areas.

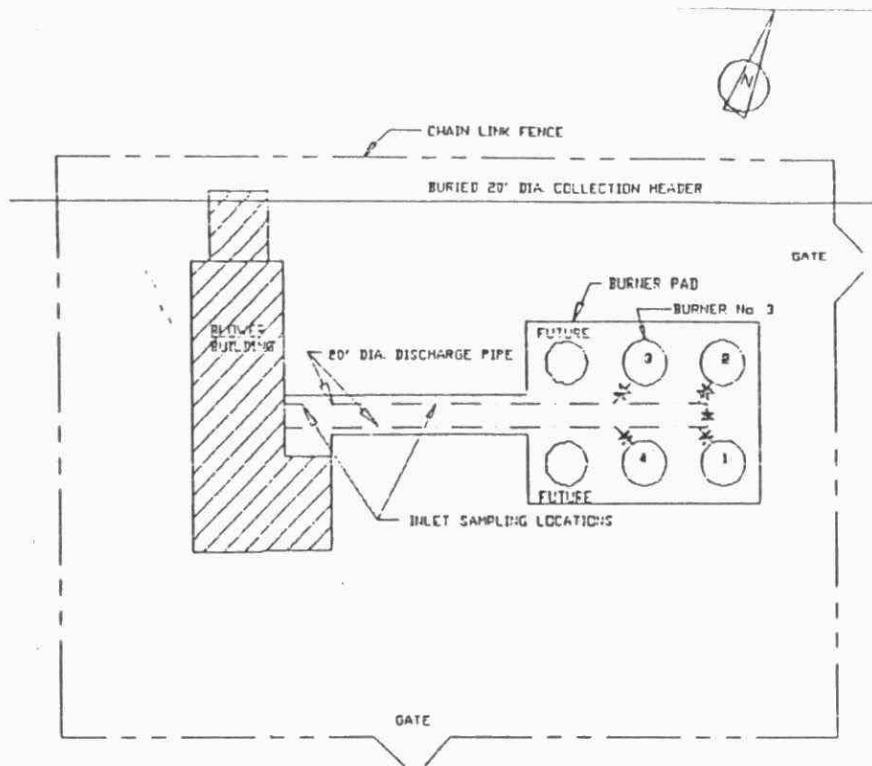
Concurrently, the operators realized that the leachate control system was filled with methane. This was venting through the cleanout manholes as well as filling the leachate pumping station. There was also evidence of methane in the ground water drain system.

In 1984 Hydrology consultants, a division of Trow Ltd, was retained by the Metropolitan Corporation to design an Odour Control system and in early 1985 contracts were awarded and construction started for the drilling of deep wells, installation of the collection headers, blower building and one (1) Gas-flare as shown on Figure 2.

The Ministry of Environment granted a preliminary approval for the installation of one (1) Gas-Flare, which required a considerable amount of emission testing under varying operating conditions before a final permit would be issued allowing the remaining five (5) Gas-Flares to be installed.

The Gas-Flare, supplied under the contract is generally configured as shown on Figure 3 and consists of a cylindrical drum of approximately 11.5 feet in diameter and 30 feet in height. Sixteen (16) sampling ports are located at various elevations to allow for the emission testing program. Sixteen (16) individual burner elements are arranged in a circular configuration and attached to a gas supply manifold. There are no controls on the Gas-Flare other than a PLC (Programmable Logic Controller) for system monitoring and safety. This type of burner is generally referred to as being an atmospheric burner.

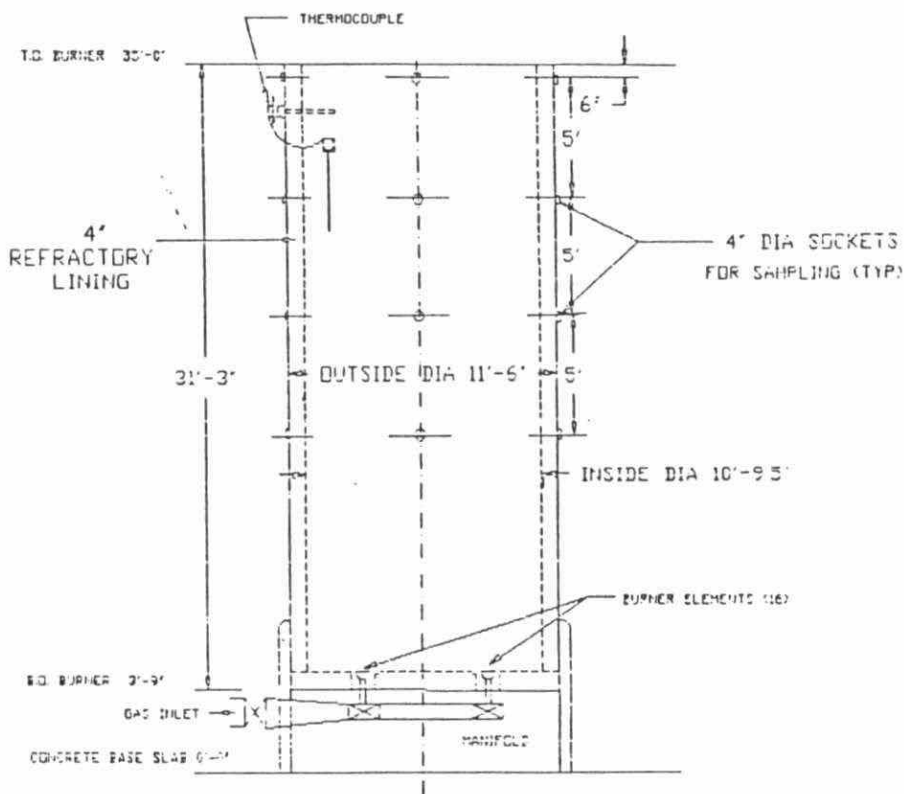
The contract was completed in April, 1986 and at a stage where the emission testing could proceed.



FLARE STATION BROCK WEST LANDFILL SITE

SCALE: 1/32" = 1'

FIGURE 2



GAS - FLARE
BROCK WEST LANDFILL SITE

SCALE 1/4" = 1'

FIGURE No. 3

EMISSION TESTING.

As mentioned earlier, traces of a large number of odorous, and potentially toxic gases are found in landfill gas. Other compounds, some of which may be toxic, (such as doixins, furans or nitrous oxides) could be the products of combustion. The creation and destruction of these various compounds is partly a function of temperature and retention time within the Gas-Flare.

The specifications required the Gas-Flare to meet, or exceed the applicable standards, guidelines and provisional guidelines of the Ontario Ministry of the Environment. Testing was to be carried out for the following list of twenty-five (25) compounds.

CO	Benzene	Dimethyl Mercaptan
CO2	Toluene	Diethyl Mercaptan
O2	Xylene	Dimethyl Sulfide
NOX	Chloroform	Dimethyl Disulfide
THC	Ethylene Dichloride	Diethyl Disulfide
TRS	Total Organic Acids	Ethyl Methyl Sulfide
PCB	Total Aldehydes	Hydrogen Sulfide
PCDD	Styrene	1,3 Butadiene
PCDF		

The MOE provided a grant, including the use of their mobile testing laboratory, to assist the Corporation in successfully completing this testing program. The reasons for the Ministries participation in this project were due to the fact that never before have landfill Gas-Flares been subject to such an extensive emission testing program, and therefore very valuable information would become available for future reference and approvals.

Preliminary test runs started in early April, 1986, with the use of the MOE mobile testing laboratory. Continuous monitoring took place for CO, CO2, O2, TRS, THC and Temperature.

Gas flow at 3400 cfm and methane concentration of approx. 45%. Very soon it became evident that this type of Gas-Flare, (atmospheric burner) would not provide a stable combustion process due to varying atmospheric pressures, wind velocity changes and fluctuations in the quality of the landfill gas.

The measured data fluctuated wildly, Total Hydro Carbon was recorded from a low of 50 ppm to a high of 3800 ppm (max. allowable 100 ppm).

Combustion temperatures were recorded at around 600 - 700 C.

The results from this first test indicated that in order to maintain a stable combustion process, some type of combustion air and gas pressure control would be required.

To satisfy ourself of the need for controls, a test was conducted with the bottom section of the Gas-Flare closed off with fire bricks, leaving a number of openings all around the perimeter which could be reduced or enlarged in size to allow for an increase or reduction of air flow to the burner elements.

A second test run was then conducted which showed a dramatic improvement over the first test. All measured variables were more stable and combustion temperatures up in the 1750 - 1850 °F. However, every time there was a change in gas flow, or gas composition to the Flare, adjustments had to be made to the size of the openings to compensate for the changed combustion air requirements.

The original specifications for the flare called for no visible flame from the top of the flare at a max. flow of 3400 cfm. With the reduced combustion air flow during the test, flames appeared from the top at irregular intervals, indicating that the flare would have to be extended for approx. another 5 feet.

We were able to justify flow rates to the Gas-Flare from a low of 2000 cfm to a max. of 3400 cfm (design flow) and methane concentrations of 25% to 55%.

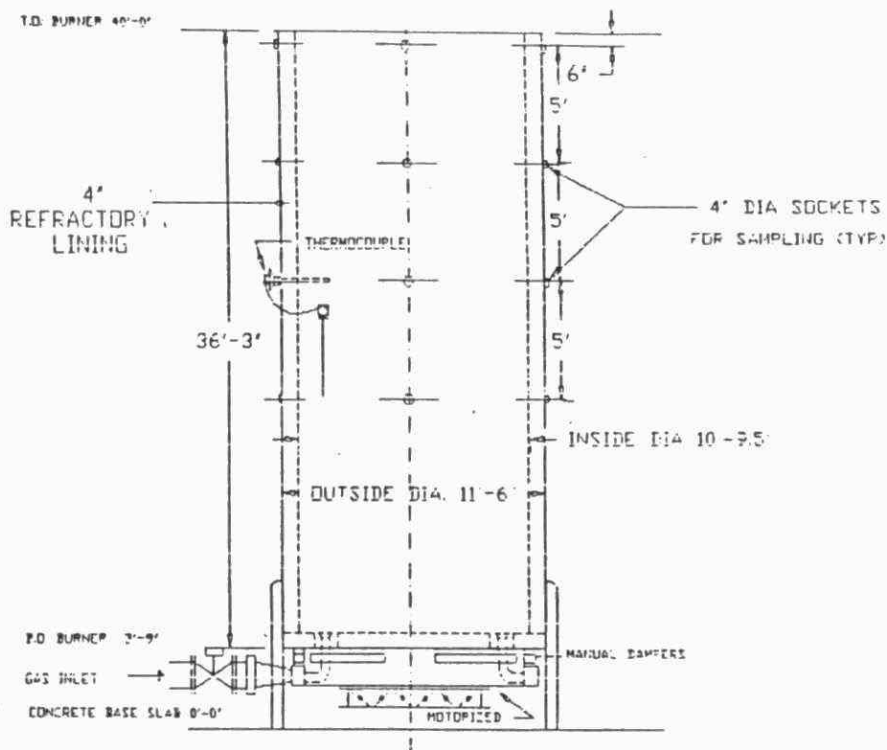
Having satisfied ourselves that modulating controls on the combustion air intake and gas flow to the flare would solve the unstable combustion process, the decision had to be made if this flare could be modified yes or no. Lengthy discussions took place between the manufacturer of the Flare (Heatco), our Consultants (Hydrology Consultants) and our Engineering staff, keeping in mind the odour complaints from the local residents.

The final decision, mainly due to odour complaints, was to leave this Flare in operation and order a second Gas-Flare with all the necessary controls in place and modify the existing flare at a later date.

The controls selected were Honeywell digital controllers model UDC-4000 for both the gas manifold pressure and combustion air control. Configuration of the new flare is as shown on figure 5, with manual dampers around the perimeter and one modulating damper in the bottom surface of the flare.

The reason for the manual dampers is to be able to make adjustments to the combustion air flow over a large range of gas flows, gas compositions and leaving the modulating damper in its control range of 25% to 75% open. Combustion air requirements are governed by a temperature sensor placed in the off-gas flow and controlling the combustion air inlet damper, as shown on Figure 4.

The complete system is under supervision by a PLC (Programmable Logic Controller), which monitors all functions such as flame out, overburn, high temperature, restart and automatic shut-down, etc. Integration of the new controllers into the PLC program was mandatory to maintain a safe and reliable system.



MODIFIED GAS - FLARE
BROCK WEST LANDFILL SITE

SCALE 1/4" = 1'

FIGURE No. 4

A new Gas-Flare was delivered to the site in late 1986 and installation started, including all required changes and additions to the PLC control system. The work was completed in late March, 1987 and preliminary testing started to calibrate the newly installed controllers. All indications during the calibration runs looked promising. Again this calibration was carried out with assistance from MOE staff and there mobile test laboratory.

The results from the preliminary test indicated that the Gas-Flare could be operated from 2000 cfm up to 3400 cfm with methane concentrations of 30% to 55%. This resulted in the selection of four different operating parameters under which the final emission testing would take place.

The following four conditions were selected:

- A: 3400 cfm and 55% CH₄.
- B: 3400 cfm and 30% CH₄.
- C: 2000 cfm and 55% CH₄.
- D: 2000 cfm and 30% CH₄.

All test runs were to be repeated twice and continuous for a four (4) hour period each.

Mann Testing Laboratories in association with Imet Inc. were selected to carry-out the full emission testing program.

Set-up and instruments calibrations took two (2) day's and all systems were ready to go on Monday, March 23, 1987.

Included in the test program was the monitoring of the incoming land fill gas for the following compounds:

- A: Hydrogen Sulfides.
- B: Methyl Mercaptans.
- C: Dimethyl Sulfide.
- E: Ethyl Mercaptan.
- F: Ethyl Methyl Sulphide.
- G: Dimethyl Disulphide.
- H: Oxygen
- I: Total Hydro Carbon.
- J: Carbon Dioxide.

The following tables summarizes the collected data for all compounds at the four different operating conditions.

Table 1.

COMPOUND.	MDL.	OUTLET. 3400 CFM. INLET		OUTLET. 3400 CFM. INLET.	
		55%-CH ₄ .		30%-CH ₄ .	
CO	%	8.6	41.4	9.6	41.2
CO ₂	ppm	21	--	12.9	--
O ₂	%	11	0.8	10.1	7.8
NO _x	ppm	16	--	17.3	--
THC	ppm	2.4	49.9 %	11.0	29.8 %
TR6	ppm	ND	--	ND	--
PCB	142 ng/m ³	ND	--	ND	--
PCDD	0.63 ng/m ³	ND	--	ND	--
PCDF	0.63 ng/m ³	ND	--	ND	--
BENZENE	0.5 ug/m ³	24.5	--	19.0	--
TOLUENE	0.5 ug/m ³	14.1	--	4.0	--
XYLENE	0.5 ug/m ³	1.0	--	--	--
CHLOROFORM	1.0 ug/m ³	--	--	--	--
ETHYLENE DICHLORIDE	1.0 ug/m ³	--	--	--	--
1,3 BUTADIENE	1.0 ug/m ³	--	--	--	--
TOTAL ORGANIC ACIDS	1.8 mg/m ³	ND	9.3	ND	TRACE
TOTAL ALDEHYDES	0.8 mg/m ³	ND	ND	ND	ND
STYRENE	0.5 ug/m ³	2.8	--	--	--
METHYL MERCAPTAN	0.01 ppm	ND	4.0	ND	4.0
ETHYL MERCAPTAN	0.01 ppm	ND	ND	ND	ND
DIMETHYL SULFIDE	0.01 ppm	ND	ND	ND	ND
DIMETHYL DISULFIDE	0.01 ppm	ND	ND	ND	ND
DIETHYL SULFIDE	0.01 ppm	ND	ND	ND	ND
ETHYL METHYL SULFIDE	0.01 ppm	ND	ND	ND	ND
HYDROGEN SULFIDE	0.01 ppm	ND	18.2	ND	22.5

Table 2.

COMPOUND.	MDL.	OUTLET, 2000 CFM. INLET 55%-CH ₄ .		OUTLET, 2000 CFM. INLET, 30%-CH ₄ .	
CO	%	9.6	41.3	9.6	29.8
CO ₂	ppm	53	--	12	--
O ₂	%	10.5	1.8	10.8	8.4
NOX	ppm	17	--	21	--
THC	ppm	4.0	48.7 %	2.3	28.4 %
TRS	ppm	ND	--	ND	--
PCB	142 ng/m ³	ND	--	ND	--
PCDD	0.63 ng/m ³	ND	--	ND	--
PCDF	0.63 ng/m ³	ND	--	ND	--
BENZENE	0.5 ug/m ³	30.6	1 mg/m ³	35.3	4 mg/m ³
TOLUENE	0.5 ug/m ³	4.3	135 mg/m ³	0.5	93 mg/m ³
XYLENE	0.5 ug/m ³	--	38 mg/m ³	1.5	71 mg/m ³
CHLOROFORM	1.0 ug/m ³	--	0	--	0
ETHYLENE DICHLORIDE	1.0 ug/m ³	--	5 mg/m ³	--	0
1,3 BUTADIENE	1.0 ug/m ³	--	0	--	0
TOTAL ORGANIC ACIDS	1.8 mg/m ³	ND	TRACE	ND	TRACE
TOTAL ALDEHYDES	0.8 mg/m ³	ND	ND	ND	ND
STYRENE	0.5 ug/m ³	0.7	--	0.6	--
METHYL MERCAPTAN	0.01 ppm	ND	3.3	ND	3.0
ETHYL MERCAPTAN	0.01 ppm	ND	ND	ND	ND
DIMETHYL SULFIDE	0.01 ppm	ND	ND	ND	ND
DIMETHYL DISULFIDE	0.01 ppm	ND	ND	ND	ND
DIETHYL SULFIDE	0.01 ppm	ND	ND	ND	ND
ETHYL METHYL SULFIDE	0.01 ppm	ND	ND	ND	ND
HYDROGEN SULFIDE	0.01 ppm	ND	17.8	ND	18.5

TABLE 3.

Contribution to the local atmosphere
from the Brock West Landfill
Gas-Flare.

Continuous gases.

FLOW, G %-METHANE.	CO. %	CO2. ppb.	NOX. ppb.	GRAB SULFUR GASES. ppb.	THC. CH4. ppb.
3400 cfm - 55%.	<0.002	1.8 ppb	2.5 ppb	ND	0.67 ppb
3400 cfm - 30%.	<0.002	1.8 ppb	3.1 ppb	ND	0.31 ppb
2000 cfm - 55%.	<0.002	8.9 ppb	2.8 ppb	ND	0.34 ppb
2000 cfm - 30%.	<0.002	3.4 ppb	3.9 ppb	ND	0.25 ppb

Note: Calculations based on the maximum plume concentration as determined using the standard Pascal & Gilford dispersion calculation.
(Reg.308, sect. 2.3 subsection 2A3 and 2B4)

From the foregoing tables it can be concluded that the modified Gas-Flare, with controls on the gas pressure and combustion air control, performs very satisfactory and provides an stable and reliable combustion process. The amount of emissions, contributed to the local atmosphere is minimal and contains no toxic or odorous compounds, resulting in a large reduction of odour complaints from the local residents.

The MOE is presently reviewing the test results before a final operational permit will be issued.

At present, four (4) Gas-Flares have been installed and are operational. Two Gas-Flares are in use, incinerating approximately 7000 cfm of collected landfill gas with a methane concentration of approx. 45% by volume.

FUTURE DEVELOPMENTS.

Since the completion of this incineration system at the Brock West Landfill Site, the landfilling operation has been proceeding. The collection system has been expanded, additional wells and trenches placed.

The landfill is expected to remain open for dumping till sometime in 1990, after which the site will be closed and proper closure proceedings will be carried-out.

In this era of energy conservation, it must be recognized that all this landfill gas constitutes a tremendous amount of energy which at present is all wasted by incineration.

At the present rate approx. 189,000,000 BTU/HR and estimated to be in 1990 approx. 270,000,000 BTH/HR.

The Metropolitan Corporation has actively investigated the possible recovery of this energy, proposals have been invited and reviewed during the past year.

Contract negotiations are at present taking place with one of the proponents for the upgrading of the landfill gas to pipe line quality gas and sale to Consumers Gas Co. Also the recovery of Carbon Dioxide is included in this proposal, making this proposal financially very attractive, both to the Contractor and the Metropolitan Corporation.

The recovery and upgrading system is expected to be in operation by the end of 1988 and early 1989.

ACKNOWLEDGEMENTS.

The Brock West Landfill Site is owned and operated by the Municipality of Metropolitan Toronto, of which Mr. D. Flynn is Chairman. The operation is under control of the Works Department of which Mr. F.J. Horgan P.Eng is Commissioner and Mr. R.G. Ferguson P.Eng is Deputy Commissioner.

Investigations, Design, Testing, Modifications and Construction supervision were a joint responsibility by Hydrology Consultants, a division of Trow Ltd. and the Metropolitan Works Departments Refuse Disposal Division and the Engineering Division.

PASSIVE DEVICES FOR THE
MEASUREMENT OF AMBIENT SULPHUR DIOXIDE

D.B. Orr¹, M.A. Lulis¹, W.H. Chan¹, N.W. Reid¹, J.C. Hipfner²
and J.E. Hunt³

Abstract - The development and application of two simple diffusion devices used to help define long-term atmospheric SO₂ concentrations is described. Laboratory testing of a Nuclepore device determined that diffusion constants (k) are independent of SO₂ concentration and dosage and k is quite reproducible. There is no dependence for k on air velocity above 2.5 m/s. Field testing of the Nuclepore and Wafer devices indicated there appears to be a concentration dependence of k when SO₂ concentrations are less than 1 ppb. When SO₂ data greater than 1 ppb are considered, calculated k values are quite reproducible within $\pm 50\%$ between sampler type and over time. A diffusion constant of $1.0 \times 10^{-5} \text{ m}^2/\text{s}$ may be assumed for these devices when monitoring for SO₂. The precision estimates associated with the Nuclepore and Wafer diffusion devices are 15% and 13%, respectively. Recommendations for future use of the devices are given.

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INTRODUCTION

Because of cost and manpower requirements to operate standard air monitoring equipment, as well as the unavailability of electrical power at many non-urban sites, the Ontario Ministry of the Environment has explored the possibility of extensively using simple, inexpensive passive diffusion devices to help define the long-term atmospheric SO_2 concentration fields across the Province. The concentration data are used to estimate SO_2 dry deposition rates in the Ministry's Acidic Precipitation in Ontario Study, as well as for assessing the long-term local impact of large sources of SO_2 emissions.

The use of passive samplers for ambient SO_2 measurement is by no means new or unique. For instance, Reiszner and West (1973) developed a sampler which made use of a gas permeable dimethylsilicone polymer membrane fitted to the end of a glass tube. The SO_2 diffused through the membrane and was fixed in a dichlorosulfiteomercurate (II) solution, and was determined subsequently by colorimetric analysis. In a later version (McDermott et al., 1979), a manganese (II) chloride - glycerol solution was used as the fixing solution. The Reiszner-West sampler was field tested at some sites in Ontario, but was deemed unsuitable due to lack of sensitivity in rural locations and to freezing of the solution during cold weather.

A modified sampler, hereafter referred to as the "Nuclepore" device, was developed by the Ministry of the Environment in 1978 as an alternative to the Reiszner-West device. It used an 8.0 micron polycarbonate filter as the gas permeable membrane and a pair of potassium carbonate/glycerol impregnated cellulose filters as the trapping agent. The polycarbonate filter had a significantly greater SO_2 diffusion rate, increasing the low level sensitivity. The impregnated filter made the extraction and analysis simpler and loss of SO_2 as a result of back diffusion negligible. There were also the added advantages of ease of handling and cold weather operation.

In the most recent attempt to improve the low level sensitivity, the Ministry of the Environment has employed a double-faced filter holder with a permeable membrane/impregnated filter pair/permeable membrane configuration. This version is referred to as the "Wafer" device.

This paper describes the laboratory and field evaluation experiments of the Nuclepore passive sampler and the field evaluation of the Wafer device. Specifically, the reproducibility of the Nuclepore sampling results will be assessed, the comparability of the Nuclepore and Wafer devices will be addressed, and the precision associated with the Nuclepore and Wafer samplers will be quantified. Based upon these observations and conclusions, a number of recommendations concerning the applicability of passive diffusion devices for ambient air monitoring can be stated.

EXPERIMENTAL SECTION

The Nuclepore sampler consisted of an open-faced 'Swin-Lok' filter holder, with a 47 mm, 8.0 micron polycarbonate Nuclepore (preliminary

field tests used Unipore) membrane to damp out eddy motions and promote molecular diffusion from the ambient air to the trapping medium. The specific properties of the Nuclepore membrane are described by Nuclepore Corporation (1984). The trapping medium consisted of two 47 mm Whatman 41 cellulose filters, impregnated with a potassium carbonate (25% W/V)/glycerol (10% V/V) solution, using a method similar to that published by Johnson and Atkins (1975). These filters were then placed between the polycarbonate membrane (in direct contact with it) and the filter support screen. The nipple of the filter pack base was sealed to promote unidirectional diffusion across the membrane.

The Wafer device consisted of a pair of 37 mm potassium carbonate/glycerol impregnated Whatman cellulose filters sandwiched between two 37 mm, 8.0 micron polycarbonate Nuclepore membranes. The filters and membranes were retained in a polyolefin snap-ring cassette - the filter cassette used in dichotomous air samplers.

Figure 1 shows the configurations of the Nuclepore and Wafer devices. It should be noted that the exposed surface areas of the two devices are roughly equivalent.

Prior to field deployment of the Nuclepore samplers, a series of experiments were carried out in the laboratory under controlled conditions to evaluate the response of the diffusion devices as a function of SO_2 concentration and dose (i.e., concentration x exposure time) and air flow rate past the sampler (UTS, 1980). A flow system was built into which the sampler could be inserted and from which SO_2 concentrations and air flow velocities could be adjusted over a wide range (in these experiments, a slightly different sampler design was used from that illustrated in Figure 1 - the impregnated filter rested on a polycarbonate membrane which was glued onto a glass tube, rather than retained in a Swin-Lok filter holder. The results are expected to be the same for both designs). Likewise, it is anticipated that the Wafer device would mirror the response of the Nuclepore sampler if subjected to the laboratory testing conditions.

Subsequent field testing of the Nuclepore sampler took place from 1982 to 1984 (Phase 1) during both warm and cold seasons at a number of sites across Ontario, where air is also routinely sampled for SO_2 on a daily basis and/or 28-day basis using the filter pack method (Chan et al., 1985 a, b). A wide range of SO_2 concentrations (from near-background in northern Ontario to relatively high values in the south) are realized at these sites. Phase 2 of field testing for both the Nuclepore and Wafer samplers was conducted during 1986 and 1987. The passive diffusion devices were colocated at a daily ambient air sampling site, cumulative (28-day) ambient air sampling sites and/or continuous monitoring sites in the Sudbury vicinity. The continuous SO_2 monitors are sensitive only to the parts per hundred million levels, not to the desirable parts per billion level. Therefore, results obtained at the continuous monitoring sites will not be reported here.

During both phases of the field testing, passive samplers were exposed over 28-day intervals at each location under the same shelter as was used for the filter packs. Duplicate samples were collected by both

the Nuclepore and Wafer samplers at selected sites and both types of devices were colocated at these sites for comparison purposes during the second phase of field testing. After exposure, the impregnated filters were unloaded from each sampler, and the mass of SO_2 that had been absorbed (m) was determined (as SO_4^{2-} in the aqueous filter extract, by ion exchange chromatography).

The purpose of the field testing was to derive an average diffusion cell constant (k). Knowing the concurrent ambient air volume-weighted average SO_2 concentration (c) as determined by the filter pack at the site, the mass of SO_2 collected (m) by the diffusion sampler and the duration of exposure (t) for the devices, k was determined using the formula $k = m/ct$. Once the two versions of passive devices have been characterized by the determination of k , this relationship allows the calculation of SO_2 concentrations. It becomes simply a matter of measuring the filter loadings and knowing the exposure period.

RESULTS AND DISCUSSION

The laboratory experiments indicated that the Nuclepore passive SO_2 samplers had diffusion constants which were independent of concentration and dosage and were reproducible, with a relative standard deviation of about 15% (UTS, 1980), based upon the results from five simultaneously exposed samplers. They showed no dependence on air velocity above about 2.5 m/s. The concentration range examined in these laboratory experiments, namely 340 to 2350 ppb, was significantly higher than that encountered in subsequent field trials.

The results of the two-phased field sampling program are plotted in Figure 2 in terms of average mass of SO_2 collected by the two types of devices versus the air concentration of SO_2 determined by the filter pack at each site. The linear regression coefficients for the expression $m(\mu\text{g}) = ac(\text{ppb}) + b(\mu\text{g})$ and the mean diffusion constants and their respective standard deviations are summarized in Table 1. The large variation in slope values, non-zero intercepts and the mean diffusion constants suggests not only are the two types of diffusion devices not equivalent in measuring SO_2 passively, but also suggests the results are not reproducible over time when the same devices are used.

However, closer scrutiny of the data reveals there is a suggestion of a concentration dependence of the diffusion constant with increasing k values for SO_2 concentrations less than about 1 ppb, as shown in Figure 3. This dependence is difficult to verify, since at such low levels there is also a large uncertainty in the air concentrations (c) measured by the filter pack, so that some of the apparent variation in k may be due to errors in c as measured by the filter pack rather than a change in the performance of the diffusion sampler at low concentrations. Furthermore, since most of the low concentrations occurred at locations in northern Ontario, the observed variation in k may be partly due to meteorological factors. The linear regression coefficients and the mean diffusion constants and standard deviations for the subset of experiments where c was greater than 1 ppb are summarized in Table 2.

The regression coefficients presented in Table 2 are to be used only for generalizing about the relationships which exist between the average mass of SO_2 collected by the diffusion devices and the concurrent ambient air SO_2 concentration. Similar slopes and intercepts for the Nuclepore and Wafer diffusion devices indicate they are roughly equivalent when used in the field to passively measure SO_2 . The discrepancies between the regression coefficients for the two phases of Nuclepore use indicate the results may not be reproducible over time. The discrepancies can be explained by the nature of the two data sets used. The data from Phase 1 are skewed towards lower concentrations and mass loadings. Two data points of high mass loading and high concentration greatly influence the determination of slope. The data used in Phase 2 were more evenly distributed over the mass loading and concentration ranges. Because of this normal distribution, the regression equation determined by Phase 2 data is probably more representative of the relationship exhibited between average mass loading and the concurrent SO_2 concentration. The key statistic from Table 2 is the mean diffusion constant. The mean diffusion constant is quite reproducible between the two types of devices and by the Nuclepore sampler over time, with an accuracy of $\pm 50\%$.

Precision estimates for the diffusion constants of the Nuclepore and Wafer devices (when all data are considered) were determined as the median absolute percentage difference of their measurements. The precision associated with the Nuclepore sampler is 15%, while the precision associated with the Wafer sample is 13%.

CONCLUSIONS

The present experiments indicate that in areas where the monthly average SO_2 concentration is expected to be greater than about 1 ppb (possibly at lower levels as well), either of the passive devices described here can be used to monitor SO_2 levels (over a sampling period of about one month) with an accuracy of roughly $\pm 50\%$. Where accuracies of this order are acceptable, such devices can be especially effective for better defining the long-term SO_2 concentration field, both over large geographical areas and around strong emission sources, at a considerably lower cost than if continuous monitors were used. If the passive samplers are constructed as described here, then a diffusion constant of $1.0 \times 10^{-5} \text{ m}^2/\text{s}$ may be assumed for use in the formula $k = m/ct$, although a calibration of the sampler against a colocated air monitor is recommended for better results.

RECOMMENDATIONS

1. The Ontario Ministry of the Environment is recommended to deploy passive SO_2 devices on a routine basis in its Acidic Precipitation in Ontario Study, particularly in the northern part of the Province where distances between active air sampling equipment can exceed hundreds of kilometers.

2. The Ontario Ministry of the Environment should implement the use of these devices around strong emission sources, notably in the Nanticoke industrial complex region, the Sudbury area and around Atikokan. However, these devices should not be used in conjunction with continuous SO_2 monitors unless the gas analysers are sensitive down to ppb levels.
3. Surrogate surface devices have been used for determining the flux of SO_4^{2-} , NO_3^- , Ca^+ and K^+ to the upper canopies of deciduous forests (Lindberg and Lovett, 1985). Applying this approach, the diffusion devices described here would be excellent surrogates for determining the flux of SO_2 to and within tree canopies. Biogeochemical studies conducted by the Ontario Ministry of the Environment would be enhanced by this approach.
4. The Ontario Ministry of the Environment should consider using diffusion devices for other gaseous compounds such as HNO_3 and NH_3 and possibly for volatile and semi-volatile organic compounds, provided a suitable absorbing medium is available for sampling.

RE1391

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Figure 1: Configuration of passive diffusion devices - Nuclepore (left) and Wafer (right)

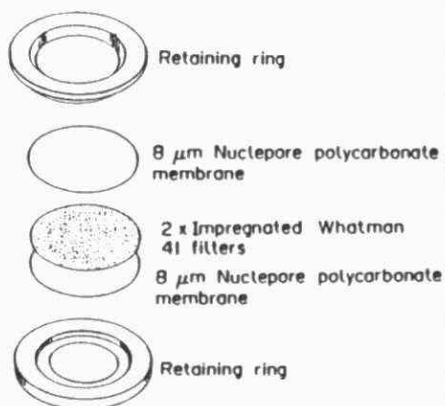
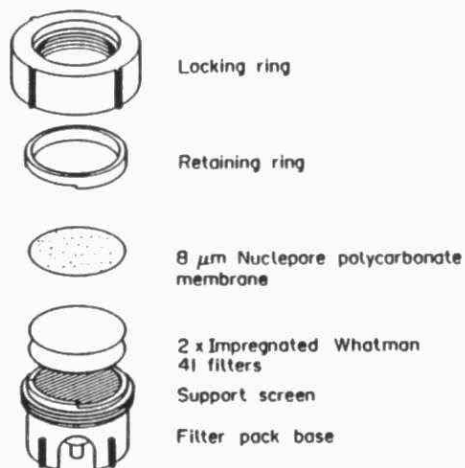
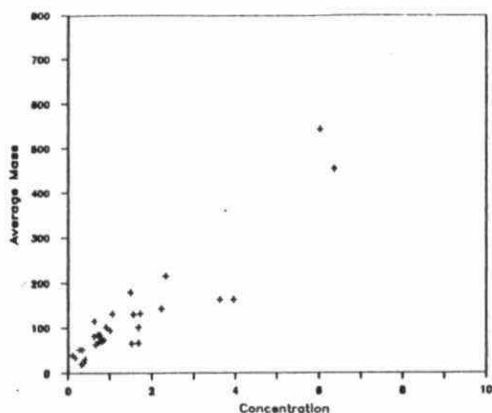
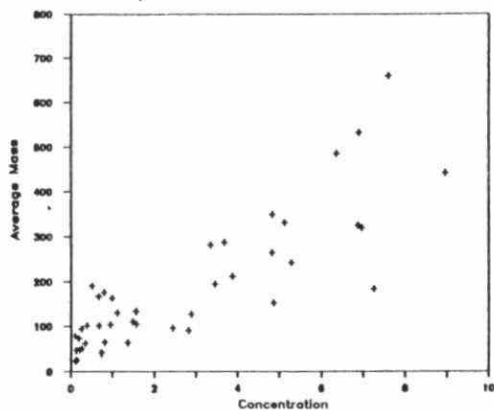


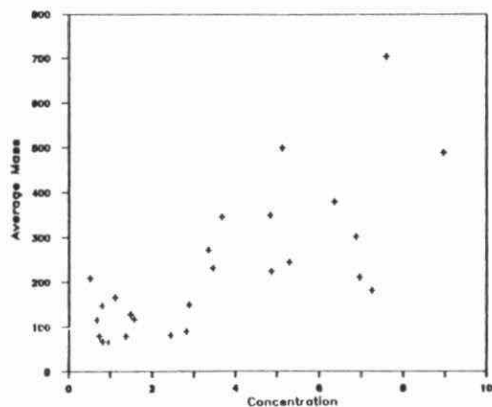
Figure 2: Average mass of SO_2 collected (μg) by diffusion devices as a function of ambient SO_2 concentration (ppb) as determined by the filter pack methods.



i) Using Nuclepore device, Phase 1

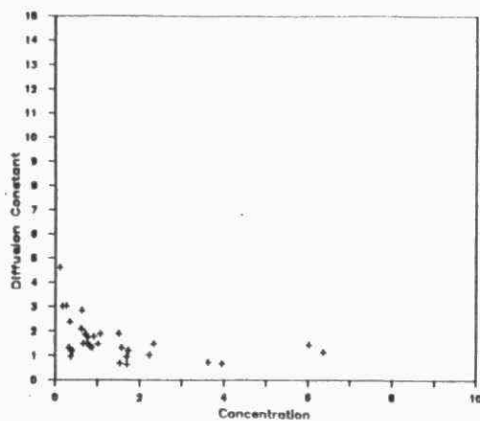


ii) Using Nuclepore device, Phase 2

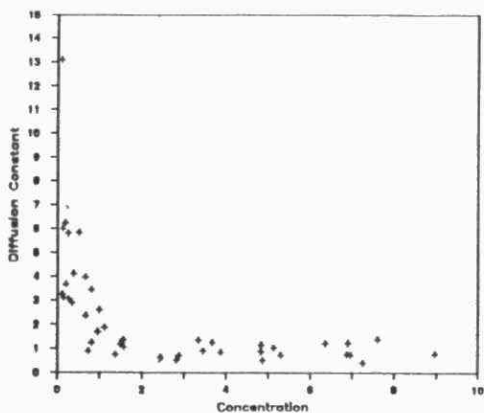


iii) Using Wafer device, Phase 3

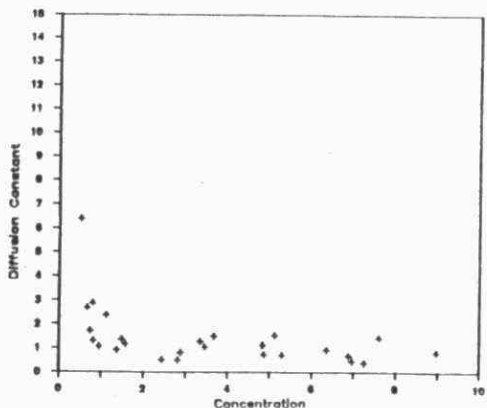
Figure 3: SO_2 diffusion constant ($\times 10^{-5} \text{ m}^2/\text{s}$) as a function of SO_2 concentration (ppb).



i) Using Nuclepore device, Phase 1



ii) Using Nuclepore device, Phase 2



iii) Using Wafer device, Phase 3

TABLE 1: Summary of Average Mass vs. SO_2 Concentration and Calculated Diffusion Constants Using All Data

Diffusion Device	n	Slope (a)	Intercept (b)	Correlation Coefficient (r)	Mean Diffusion k ($\times 10^{-6} \text{ m}^2/\text{s}$)	Standard Deviation of k ($\times 10^{-6} \text{ m}^2/\text{s}$)
Nuclepore, Phase 1	31	66.7	10.3	0.92	1.6	0.9 (74)
Nuclepore, Phase 2	42	47.4	56.0	0.84	2.3	2.4 (86)
Wafer, Phase 2	26	44.9	68.1	0.74	1.4	1.2 (88)

Values in parentheses indicate percentage of k values which lie within 1 standard deviation of the mean k value.

TABLE 2: Summary of Average Mass vs. SO_2 Concentration and Calculated Diffusion Constants Using SO_2 Concentration Data >1 ppb

Diffusion Device	n	Slope (a)	Intercept (b)	Correlation Coefficient (r)	Mean Diffusion k ($\times 10^{-6} \text{ m}^2/\text{s}$)	Standard Deviation of k ($\times 10^{-6} \text{ m}^2/\text{s}$)
Nuclepore, Phase 1	14	71.7	- 1.3	0.89	1.2*	0.4 (57)
Nuclepore, Phase 2	25	51.5	32.0	0.79	1.0*	0.5 (88)
Wafer, Phase 2	20	47.8	51.3	0.69	1.0*	0.5 (70)

Values in parentheses indicate percentage of k values which lie within 1 standard deviation of the mean k value.

*t-tests indicate that there is no significant difference between the means.

Laboratory Scale Testing Program to Develop
Understanding of a
Photochemical Flue Gas Treatment Process

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R.B. Caton, K. Smith*

Paper Presented to the 1987 Technology Transfer
Conference - Ontario Ministry of Environment
Sponsored Projects

October 1987

*Ontario Ministry of the Environment

Concord Scientific Corporation

INTRODUCTION

The occurrence of acid rain has been well documented over the past decade. The consensus is that the precursors are oxides of sulphur and nitrogen. Once emitted to the atmosphere, these gases gradually convert to sulphuric and nitric acids. These chemical changes are effected by solar radiation and the presence of other constituents. The reactions are, however, relatively slow and can take days to go to completion. During this period of time, air masses can move considerable distances. Hence the widespread impact of acid rain well beyond sources of primary emissions.

Due to the nature of the acid rain problem solutions appears to require reduction in emitting activities or containment at source. A significant contributor to atmospheric emissions in N.E. United States and Eastern Canada is the combustion of coal in electrical power generating plants. Technologies currently in use for the removal of sulphur and nitrogen oxides from coal-fired power plants are very expensive to build and operate, and produce waste products which often present significant disposal difficulties. Many technologies under development or in use focus on sulphur oxide removal only.

Concord Scientific Corporation has developed a technology for the removal of both SO_2 and NO_x from flue gas streams. The process is patented in Canada, U.S.A., and the major EEC countries. Patents are pending in Japan. A techno-economic assessment based on scientific and market research to date, carried out according to a standard approach specified by the U.S. Electric Power Research Institute (EPRI), has demonstrated that the projected capital and operating costs of the Concord Flue Gas Treatment (CFG T) process are competitive with other technologies in use or under development.

Recognizing that the main technical difficulty in controlling emissions is associated with removing sulphur and nitrogen in the forms of SO_2 and NO_x , the CFG T process uses intense far ultraviolet light to

rapidly convert these compounds to H_2SO_4 and HNO_3 . These acids are then removed from the flue gas either as acids or their salts. The result is potentially marketable by-products.

Research on the process to date has comprised extensive bench-scale experiments and detailed numerical simulation modelling of the photochemical kinetics at approximately room temperature (25 to 30°C).

Two variables which exert significant influence on the process economics are U.V. lamp efficiency at the wavelengths of interest and photon yield. Low pressure mercury lamps appear to be the best light source, however, currently available lamps need to be optimized for this particular process application. The work on lamp optimization is currently in progress by Brown Boveri in Switzerland.

In order to proceed with the development program, a better understanding of the photochemical processes taking place at elevated temperature (200-250°C) typical of flue gas streams is necessary. The design, construction, and application of a laboratory scale system along with modelling comparisons is the subject of this project.

GENERAL DESCRIPTION OF THE PROCESS

The basis of the Concord FGT Process is inherently simple. It relies on the use of ultraviolet radiation to rapidly convert NO_x and SO_2 to other chemical forms which are relatively easy to remove from the gas stream prior to emission to the atmosphere. Essentially, the process represents a rapid acceleration of chemical changes which would take place in the atmosphere - if the pollutants were released. The underlying chemical and physical processes are well understood due to several decades of research into urban smog problems for which most of the reactions of concern are similar.

Five operational configurations are possible in designing the system for a particular combustion source. The choice of the most appropriate

configuration will depend on various factors which, in most instances, are site dependent. In all configurations, the basic irradiation section is similar and consists of intense ultraviolet light sources which cause rapid chemical reactions to occur in the gas stream. Figure 1, and Figure 2 illustrate schematically, the configuration options.

Configuration A (Figure 1)

In this configuration, ammonia (NH_3) feedstock is injected into the treated gas stream following the irradiation section. The H_2SO_4 and HNO_3 are converted into their corresponding ammonium salts, $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , which are removed as particulate matter from the gas stream prior to emission.

Configuration B (Figure 1)

This is similar to Configuration A with the exception that instead of NH_3 injection following the U.V. Reactor (as shown in Figure 1), it is added prior to the irradiation section. The NO_x in the gas stream is partially converted to N_2O and N_2 (harmless gases which are vented to the atmosphere) and the remainder to ammonium nitrate (NH_4NO_3), a fertilizer by-product. The SO_2 in the gas stream is converted to ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ which is also a fertilizer by-product. Both the NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ are removed as particulate matter from the gas stream.

Configuration C (Figure 2)

In this Configuration, no NH_3 is used. All of the NO_x and SO_2 is converted to nitric acid and sulphuric acids in the irradiation zone. These acids are then removed by the use of available scrubbing process technologies, using either wet or dry systems.

FIGURE 1: CONCORD FGT PROCESS
WITH NH_3 ADDITION

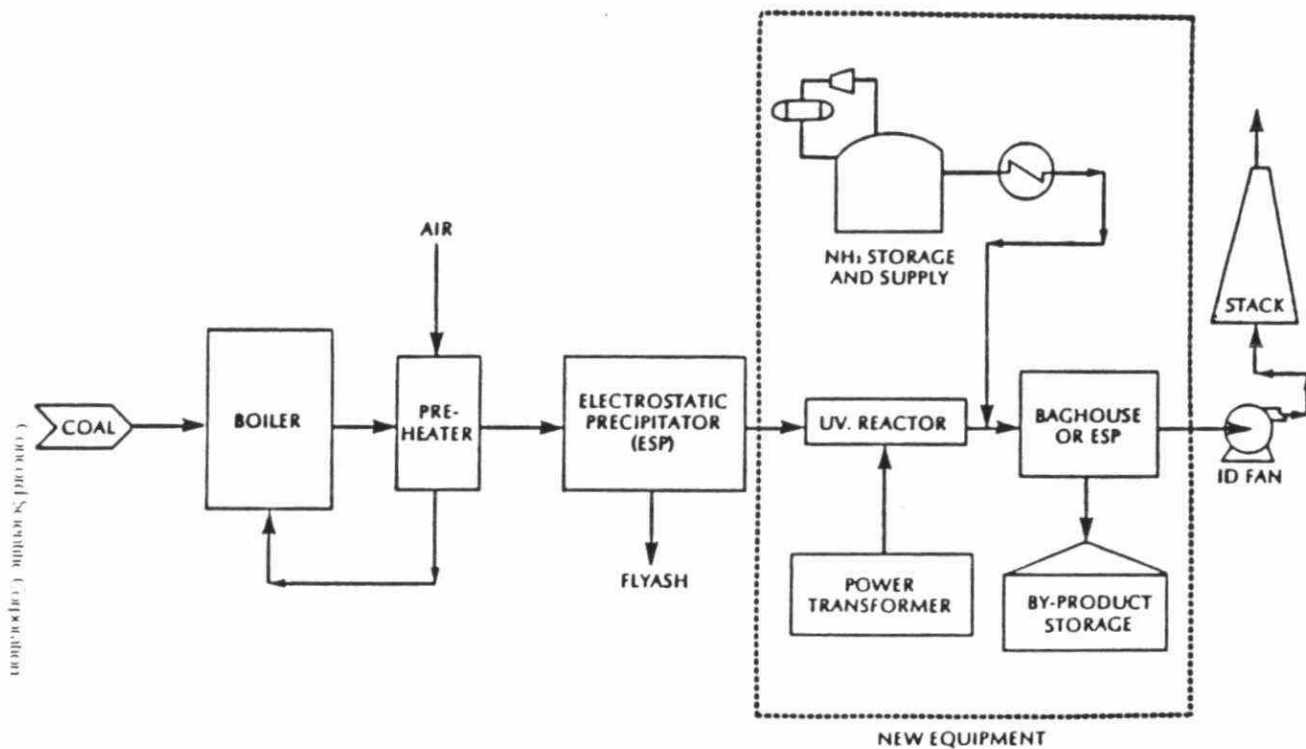
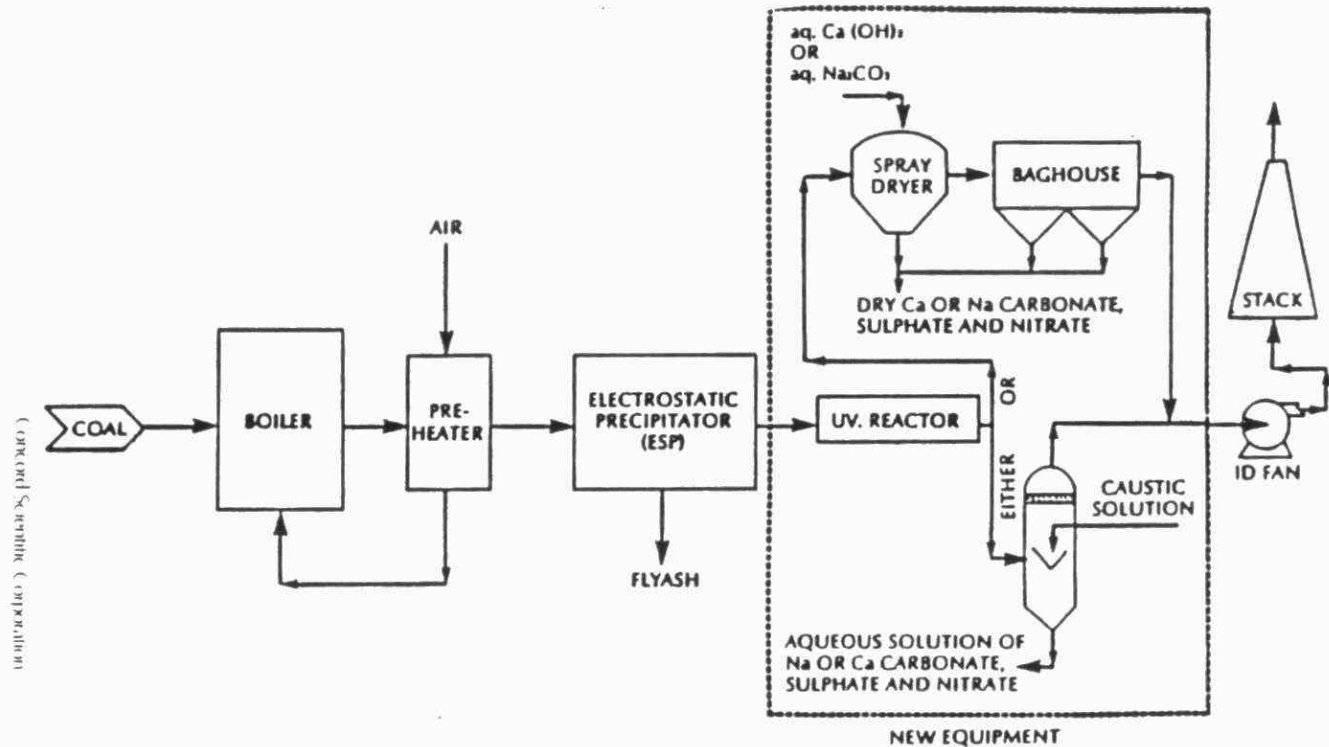


FIGURE 2: CONCORD FGT PROCESS
WITHOUT NH_3 ADDITION



Configuration D (Figure 2)

In cases where the power plant is located near ocean coastal areas, sea water scrubbers may be used. This is similar to Configuration C except that instead of the use of spray dryers or caustic scrubbers as shown in Figure 2, wet scrubbers using sea water remove the acids which are then discharged directly from the plant.

Configuration E (Figure 2)

This configuration is similar to Configuration C, except that the formed acids from the U.V. Reactor are removed in acid mist precipitators.

CHEMICAL BASIS OF PROCESS

The chemical reaction mechanism is driven by several photochemical reactions initiated by high intensity U.V. radiation. A large number of "dark" reactions subsequently take place. Most of these reactions and their rate constants have been studied extensively over the past several decades as a result of interest in understanding urban smog formation.

A chemical model, consisting of some eight photochemical reactions and fifty-five other reactions, was constructed to describe the system. These are detailed in the Appendix. Since a low pressure mercury arc is the light source of choice, the two major emission lines (185 nm and 254 nm) were used in the model. Some of the reactions are temperature dependent. Examples of rate constants at 25°C and 204°C are listed in the Appendix as well.

The major characteristics of the chemical mechanism represented by the model may be summarized as follows.

- The free radical species HO_2 and OH predominate in the removal of both SO_2 and NO_x .
- SO_2 removal occurs within the propagation steps of a free radical chain reaction, principally by the reaction:



- NO_x removal involves termination of the free radical chains.
- Where NH_3 is present, a significant fraction of NO_x is removed by reaction with NH_2 to form N_2 and N_2O .
- Quantum yields for the system should increase with temperature.

ROOM TEMPERATURE EXPERIMENTS

Experiments have been carried out at approximately ambient laboratory temperature in a cylindrical, continuous-flow, quartz reactor into which controlled mixtures of gases were introduced. The relationships between the kinetics of the reacting components and experimental conditions were determined.

Figure 3 and Figure 4 illustrate the basic experimental arrangement. In these figures, a spiral lamp is shown. Many of the experiments were also run using several linear lamps placed around the reactor.

To test the chemical model for reactions between NO_x and NH_2 , flow gases consisted of only N_2 , NH_3 and NO_x (Figure 3). Results confirmed model predictions. Photolysis of NH_3 produces NH_2 resulting in a product mix of essentially N_2O and N_2 . Most of the room temperature experiments focused on the reactor configuration shown in Figure 4 where humidified air was mixed with SO_2 and in some cases also NO_x .

FIGURE 3: EXPERIMENTAL CONFIGURATION - NO/NH₃ SYSTEM

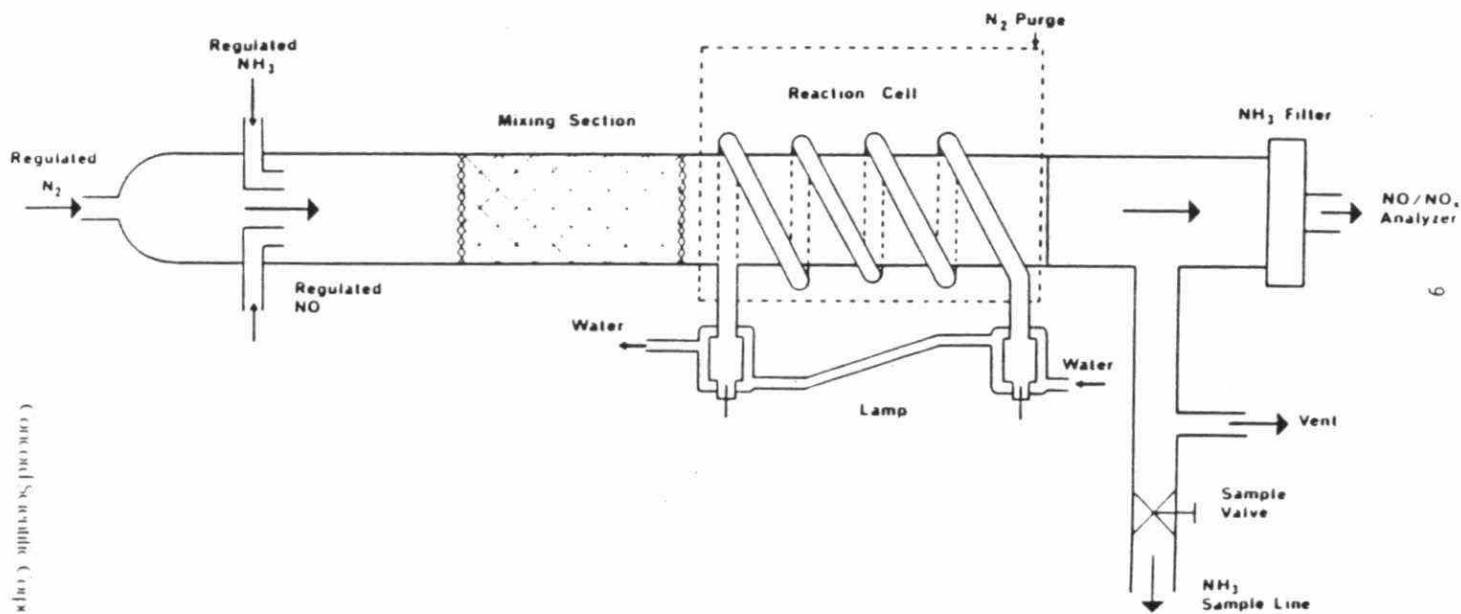
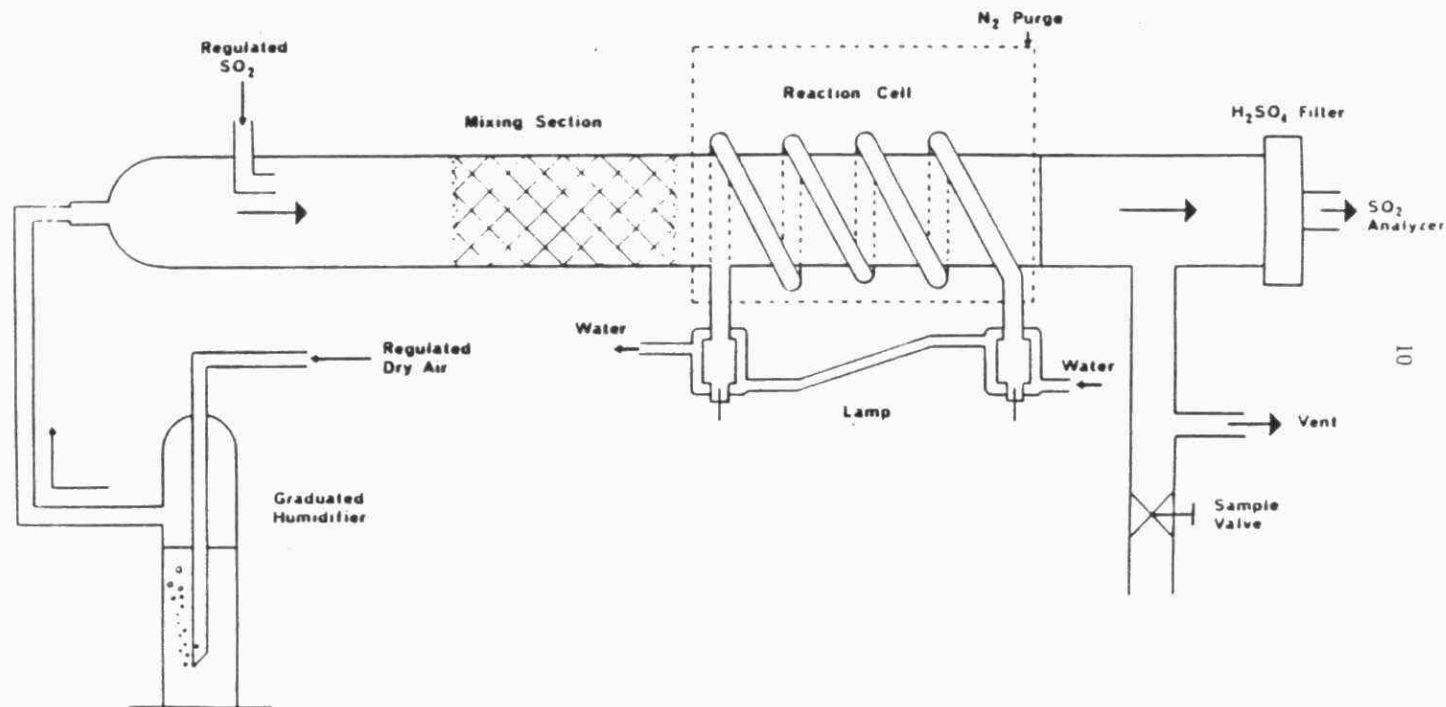


FIGURE 4: EXPERIMENTAL CONFIGURATION - SO_2 SYSTEM



The experiments performed tested the effect of physical variables such as contact time, light intensity and reaction mixture composition on removal efficiency and quantum yields. The variables tested included:

- SO_2 concentration: 100 to 2000 ppm;
- NO_x concentration: 50 to 500 ppm;
- O_2 concentration: 5 to 20%;
- CO_2 concentration: 0 and 3%;
- H_2O concentration: 0 and 5%;
- temperature: $25^\circ\text{C} \pm 5^\circ\text{C}$;
- residence time: 1 to 40 s; and
- light intensity (at 185 nm): 1×10^{13} to 4×10^{15} photons $\text{cm}^{-2}\text{s}^{-1}$.

A gas-phase, continuous flow chemical actinometer developed by Concord Scientific was used to calibrate the absolute light intensity at 185 nm in the reaction cell under physical conditions identical to those of the photochemical experiments themselves. In this actinometer, a known inlet concentration of nitrous oxide produces an outlet concentration of nitric oxide that is directly related to the intensity of U.V. light in the reactor. The nitric oxide produced is measured with a continuous NO_x analyzer. Actinometry was performed frequently interspersed with experimental runs.

In mixed systems of both NO_x and SO_2 , it was found that NO_x was removed most rapidly. Significant removal of SO_2 occurs only after depletion of NO_x . In most cases, the removal rate and efficiency observed experimentally agreed with model predictions.

Analysis of room temperature experimental data demonstrated that first-order kinetics applies to the removal of SO_2 over a range of experimental conditions with a high degree of confidence. The first-order rate constant was found to depend most strongly on the incident light intensity at 185 nm, as measured by chemical actinometry. The next most influential factor affecting the rate constants was the water

vapour concentration; but, at concentrations greater than 2%, little effect was noted. Oxygen concentration was found to have a lesser effect on the rate constant and other experimental variables and conditions had no distinguishable effect.

The quantum yield for 90% reduction of typical flue gas concentrations (i.e., 2000 ppm SO_2 initially) was found to be about 9.

Over the range of light intensities tested, the quantum yield depended inversely, but weakly so, upon incident light intensity for the range of experimental conditions. It is possible to trade off light intensity and contact time in optimizing the system.

An implication of the observed first-order kinetics behaviour is that the quantum yield increases with increased initial SO_2 concentration, so that process efficiency is greater for flue gases containing higher SO_2 concentrations.

HIGH TEMPERATURE EXPERIMENTS

The current project work programme is to design, assemble and operate an experimental system to test the CFGT process over temperature ranges up to those typically found in power plant flue gas streams (200°C-250°C). Operation of the system would systematically evaluate the influence of various conditions on the conversion kinetics for a variety of test gas mixtures and test the numerical simulation model for elevated temperature and various gas mixtures. The results will be evaluated to derive basic relationships of importance to understanding the fundamental chemical process in the test gas mixtures.

At the time of writing this paper, the apparatus has been designed, built and tested, and the desired experimental runs completed. The collected data are in the process of analysis and interpretation.

The target range of experimental parameters was as listed below.

Flue Gas Composition	O ₂	3 to 6%
	N ₂	85 to 90%
	CO ₂	1 to 3%
	H ₂ O	2 to 10%
Acid Gas Composition	SO ₂	1000 to 3000 ppm
	NO/NO ₂	200 to 400 ppm
Contact Time		1 to 6 seconds
Photon Flux (185 nm)		10 ¹⁴ to 10 ¹⁶ photons/cm ² /s
Temperature		25°C to 225°C

Data are being analyzed to determine significant dependencies. The most important include:

- effects of light intensity on reaction rate constants;
- effects of major components particularly O₂ and H₂O;
- effects of concentrations for SO₂ and NO/NO_x on reaction rate constants;
- effects of temperature on reaction rate constants; and
- effects of each of these variables on quantum yields.

Other aspects of the data are also being examined but the relationships defined above should basically characterize kinetics and quantum yields and, particularly, permit evaluation of the impact of elevated temperature on the process.

The reactor system is shown in Figure 5, and Figure 6. It consists of a quartz double wall reactor with a central channel holding a heater element. The outer space is evacuated to minimize heat transfer. Inlet gases are preheated to the desired temperature prior to entering the reaction cell. The central heating element in the cell adds sufficient heat to the gases to maintain constant temperature along the reaction path.

Twenty low-pressure mercury lamps are positioned around the reaction cell and are held by a stainless steel housing which is water-cooled. Cooling fins run next to each lamp to help maintain them at their required operating temperature. This design allows the photolysis lamps to be placed quite close to the reaction cell without compromising the required different operating temperatures of the lamps and reactor cell.

The stainless steel housing is hinged to allow access to the lamps and reaction cell. When closed, the mating surfaces are sealed with a gasket. The internal space around the lamps is purged with pure nitrogen during operation to avoid loss of U.V. light due to absorption. The nitrogen purge also provides cooling for the lamps.

Provision was included in the reactor cell to allow a sampling probe to be moved along the interior of the cell for the purpose of extracting samples of gas at any point as well as to measure temperature.

The reactor system, combined with the gas handling and mixing systems, operated extremely well. Once a desired temperature was achieved, it could be easily maintained with excellent stability. Careful testing and QA/QC procedures assured good data from the experimental runs which followed.

FIGURE 5: QUARTZ REACTOR/LAMP CONFIGURATION

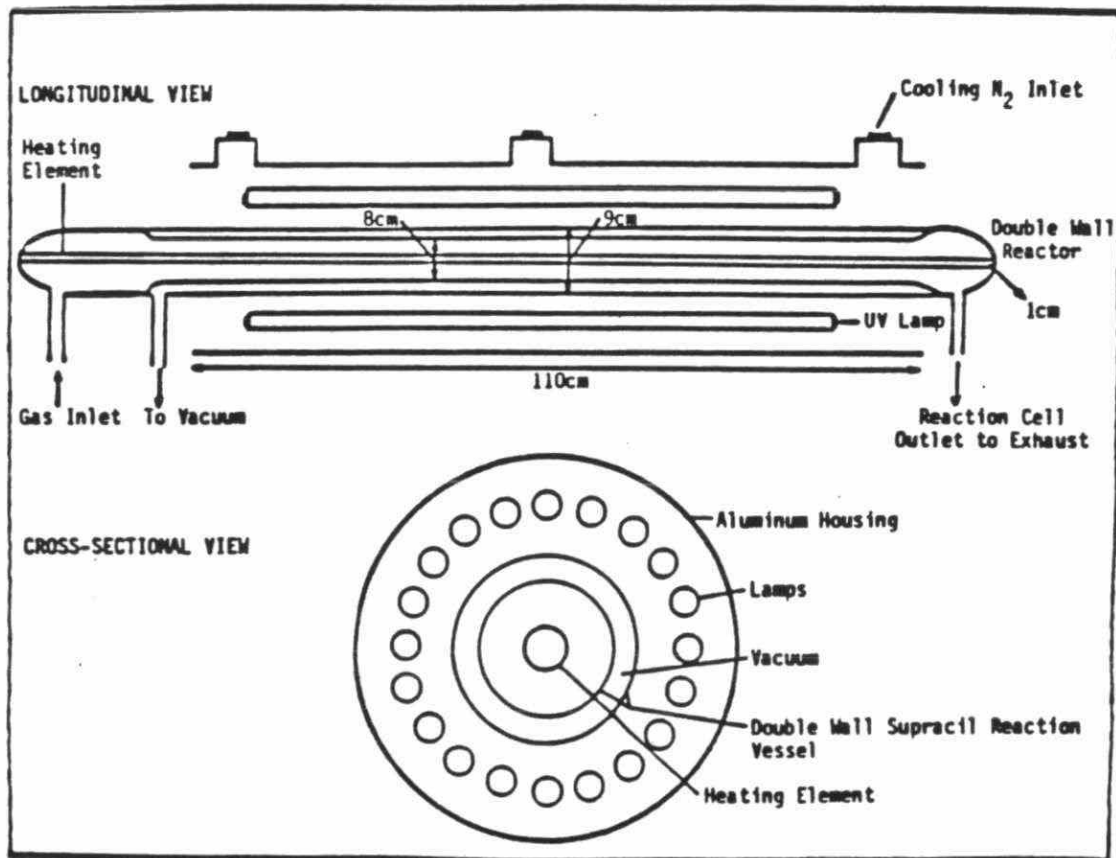
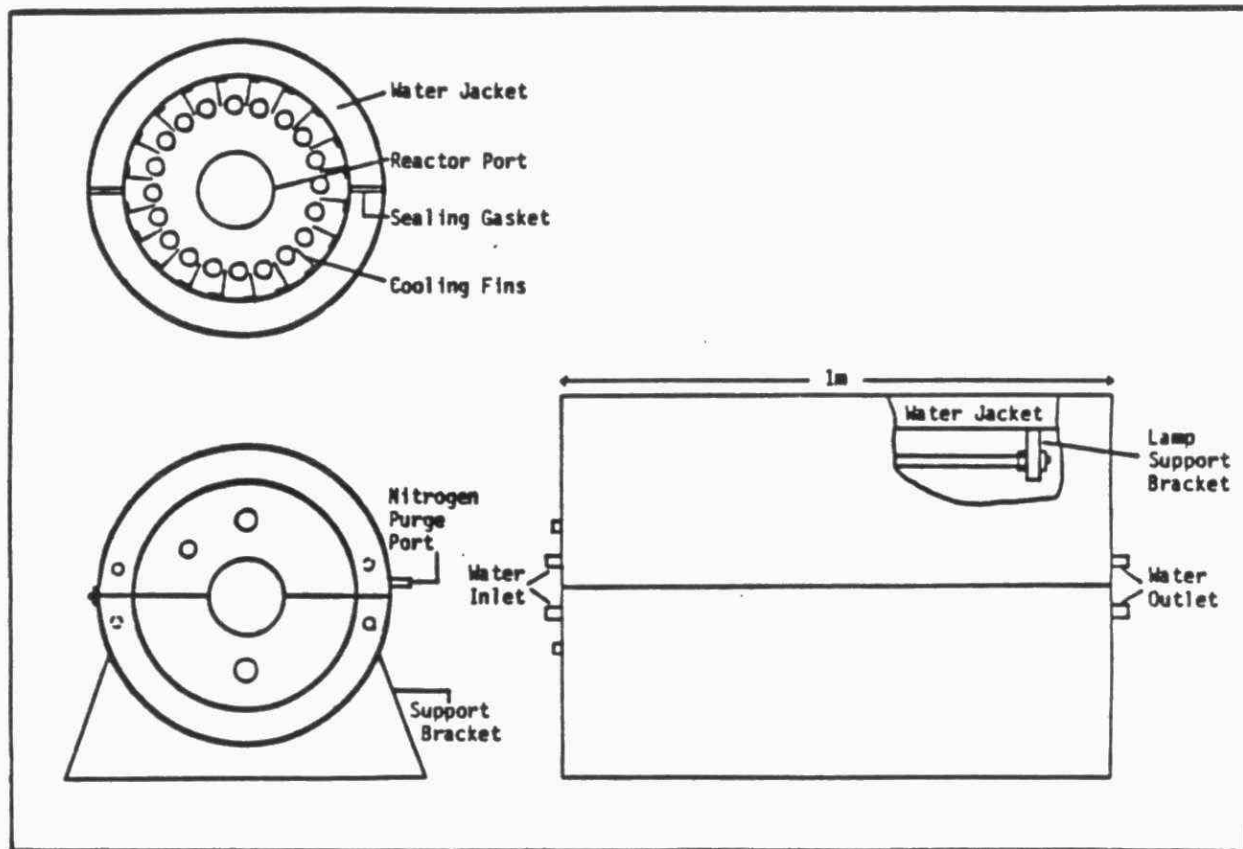
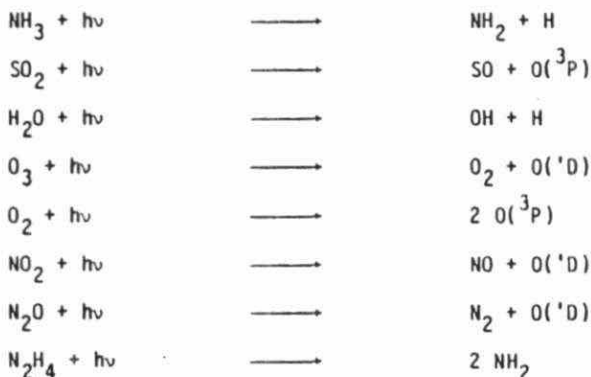


FIGURE 6: STAINLESS STEEL HOUSING FOR REACTOR SYSTEM



APPENDIXThe Reaction MechanismPhotolysesReactionsRate ConstantRef. $(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$

- | | | |
|--|----------------------|---|
| 1. $\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$ | 1.3×10^{10} | a |
| 2. $\text{NH}_2 + \text{NO}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$ | 1.3×10^{10} | b |
| 3. $\text{NH}_2 + \text{NH}_2 = \text{N}_2\text{H}_4$ | 1.5×10^{10} | c |
| 4. $\text{NH}_2 + \text{O}_2 = \text{NO} + \text{H}_2\text{O}$ | 1.2×10^3 | d |
| 5. $\text{NH}_2 + \text{RH} = \text{NH}_3 + \text{R}$ | 5.0×10^4 | e |

<u>Reactions</u>	<u>Rate Constant</u>	<u>Ref.</u>
6. $\text{NH}_2 + \text{H} = \text{NH}_3$	1.0×10^{11}	c
7. $\text{NH}_2 + \text{H}_2 = \text{NH}_3 + \text{H}$	8.7×10^2	b
8. $\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$ OR $\text{HO} + \text{NH}$	2.1×10^9	b
9. $\text{NH}_2 + \text{OH} = \text{HNO} + \text{H}_2$ OR $\text{NH} + \text{H}_2\text{O}$	6.0×10^7	h
10. $\text{NH}_2 + \text{HO}_2 = \text{HNO} + \text{H}_2\text{O}$	2.0×10^8	f
11. $\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	3.0×10^8	g
12. $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	1.0×10^8	g
13. $\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	4.0×10^5	f
14. $\text{NH}_3 + \text{HO}_2 = \text{NH}_2 + \text{H}_2\text{O}_2$	1.0×10^5	g
15. $\text{O} + \text{NO}_2 = \text{O}_2 + \text{NO}$	5.6×10^9	h
16. $\text{O}(^1\text{D}) + \text{N}_2\text{O} = \text{N}_2 + \text{O}_2$	4.5×10^{10}	h
17. $\text{O}(^1\text{D}) + \text{N}_2\text{O} = 2\text{NO}$	5.2×10^{10}	h
18. $\text{O} + \text{O}_2 = \text{O}_3$	8.7×10^6	h
19. $\text{O} + \text{NO} = \text{NO}_2$	9.9×10^8	h
20. $\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$	1.0×10^7	h
21. $\text{O}(^1\text{D}) + \text{H}_2\text{O} = 2 \text{OH}$	1.3×10^{11}	h
22. $\text{O}(^1\text{D}) (+\text{M}) = \text{O}(^3\text{P}) (+\text{M})$	$8.2 \times 10^8 \text{ s}^{-1}$ at 1 Atm.	h
23. $\text{H} + \text{O}_2 = \text{HO}_2$	8.0×10^8	h
24. $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$	5.0×10^9	h
25. $\text{O} + \text{SO} = \text{SO}_2$	5.0×10^7	b
26. $\text{O}_2 + \text{SO} = \text{SO}_2 + \text{O}(^3\text{P})$	5.0×10^4	h

Reactions	Rate Constant	Ref.
27. $O_3 + SO \rightarrow SO_2 + O_2$	4.5×10^7	h
28. $SO + SO \rightarrow SO_2 + S$ OR $(SO)_2$	2.0×10^6	h
29. $OH + OH \rightarrow H_2O + O(^3P)$	1.1×10^9	h
30. $OH + NO_2 \rightarrow HNO_3$	3.8×10^{10}	h
31. $O + O_3 \rightarrow 2O_2$	5.7×10^6	h
32. $OH + CO \rightarrow CO_2 + H$	9.0×10^7	h
33. $SO + NO_2 \rightarrow SO_2 + NO$	8.5×10^9	h
34. $H + HO_2 \rightarrow H_2 + O_2$	8.4×10^9	h
$\rightarrow 2OH$	1.9×10^{10}	h
$\rightarrow H_2O + O$	5.7×10^8	h
35. $O + OH \rightarrow O_2 + H$	2.3×10^{10}	h
36. $OH + HO_2 \rightarrow H_2O + O_2$	2.1×10^{10}	h
37. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.4×10^9	h
38. $O_3 + OH \rightarrow HO_2 + O_2$	4.9×10^7	h
39. $O_3 + HO_2 \rightarrow OH + 2O_2$	1.2×10^6	h
40. $OH + SO_2 \rightarrow HSO_3$	6.6×10^8	h
41. $H + O_3 \rightarrow OH + O_2$	1.7×10^{10}	h
42. $O + HO_2 \rightarrow OH + O_2$	1.9×10^{10}	h
43. $O + O \rightarrow O_2$	6.9×10^7	b

Reactions	Rate Constant	Ref.
44. $O + H = OH$	2.9×10^8	b
45. $H_2 + O = OH + H$	4.0×10^3	b
46. $SO_2 + O = SO_3$	1.1×10^7	b
47. $O + CO = CO_2$	3.0×10^4	b
48. $N_2H_4 + H = N_2H_3 + H_2$	1.1×10^8	b
49. $OH + H = H_2O$	7.2×10^9	b
50. $OH + H_2 = H_2O + H$	3.9×10^6	b
51. $SO_2 + HO_2 = SO_3 + OH$	5.4×10^5	b
52. $O + NO = N + O_2$	7.7×10^4	b
53. $NO + H = HNO$	8.3×10^8	b
54. $NO_2 + H = NO + OH$	7.5×10^{10}	b
55. Free radical \rightarrow wall termination	7.5×10^{-2}	i

Note 1: Many of these reactions are third order at atmospheric pressure. A pseudo-second order rate constant is quoted, and was obtained by substituting one atmosphere pressure for the third body.

2: In practice, wall termination was applied only to NH_2 radicals to ensure a conservative result.

References

- a) Lesclaux et al., 1975.
- b) Hampson & Garvin, 1977.
- c) Khe et al., 1977.
- d) Lesclaux and Demissy, 1977.
- e) Khe & Lesclaux, 1976.
- f) Estimated following Benson, 1976.
- g) Levy, 1980.
- h) Baulch et al., 1980.
- i) Based on fluid flow calculations for reactor geometry.

Temperature Dependence of Rate Constants

Reaction		k_{25}	k_{204}
$\text{NH}_2 + \text{RH}$	$\longrightarrow \text{NH}_3 + \text{R}$	2.04×10^5	3.11×10^6
$\text{NH}_3 + \text{OH}$	$\longrightarrow \text{NH}_2 + \text{H}_2\text{O}$	9.50×10^7	2.60×10^8
$\text{NH}_3 + \text{O}$	$\longrightarrow \text{NH}_2 + \text{OH}$	5.99×10^4	2.69×10^6
$\text{O} + \text{O}_2 + \text{M}$	$\longrightarrow \text{O}_3 + \text{M}$	8.84×10^6	2.91×10^6
$\text{O} + \text{NO} + \text{M}$	$\longrightarrow \text{NO}_2 + \text{M}$	1.00×10^9	4.26×10^8
$\text{O}(\text{1D}) + \text{M}$	$\longrightarrow \text{O}(\text{3P}) + \text{M}$	1.23×10^9	1.08×10^9
$\text{H} + \text{O}_2 + \text{M}$	$\longrightarrow \text{HO}_2 + \text{M}$	9.30×10^8	5.81×10^8
$\text{HO}_2 + \text{NO}$	$\longrightarrow \text{NO}_2 + \text{OH}$	5.07×10^9	3.94×10^9
$\text{O}_2 + \text{SO}$	$\longrightarrow \text{SO}_2 + \text{O}$	5.58×10^4	3.56×10^5
$\text{O}_3 + \text{SO}$	$\longrightarrow \text{SO}_2 + \text{O}_2$	3.74×10^7	1.49×10^8
$\text{OH} + \text{NO}_2$	$\longrightarrow \text{HNO}_3$	3.87×10^{10}	1.09×10^{10}
$\text{O} + \text{O}_3$	$\longrightarrow \text{2O}_2$	5.71×10^6	1.01×10^8
$\text{O}_3 + \text{OH}$	$\longrightarrow \text{HO}_2 + \text{O}_2$	3.98×10^7	1.40×10^8
$\text{O}_3 + \text{HO}_2$	$\longrightarrow \text{OH} + \text{2O}_2$	1.12×10^6	2.39×10^6
$\text{OH} + \text{SO}_2$	$\longrightarrow \text{H}_2\text{SO}_4 + \text{HO}_2$	4.96×10^9	1.27×10^9
$\text{H} + \text{O}_3$	$\longrightarrow \text{OH} + \text{O}_2$	1.68×10^{10}	3.08×10^{10}
$\text{O} + \text{O} + \text{M}$	$\longrightarrow \text{O}_2 + \text{M}$	7.87×10^7	3.07×10^7
$\text{H}_2 + \text{O}$	$\longrightarrow \text{OH} + \text{H}$	2.10×10^3	6.63×10^5
$\text{SO}_2 + \text{O}$	$\longrightarrow \text{SO}_3$	2.26×10^7	7.96×10^7
$\text{O} + \text{CO}$	$\longrightarrow \text{CO}_2$	6.98×10^4	1.09×10^6
$\text{N}_2\text{H}_4 + \text{H}$	$\longrightarrow \text{N}_2\text{H}_3 + \text{H}_2$	1.06×10^8	4.80×10^8
$\text{OH} + \text{H}$	$\longrightarrow \text{H}_2\text{O}$	1.11×10^{10}	4.34×10^9
$\text{OH} + \text{H}_2$	$\longrightarrow \text{H}_2\text{O} + \text{H}$	4.34×10^{10}	8.17×10^7
$\text{NO} + \text{H}$	$\longrightarrow \text{HNO}$	6.65×10^8	4.56×10^8
$\text{NO}_2 + \text{H}$	$\longrightarrow \text{NO} + \text{OH}$	7.71×10^{10}	1.36×10^{11}

ABSTRACT

The evaluation of a comprehensive model gives rise to a number of problems which include those associated with uncertainties in the data used to run and evaluate the model. Additionally, the inherent complexity of the model makes it difficult to ascribe discrepancies between model predictions and observations to any one source (or several sources) of errors. This paper shows that the solution of these problems requires an iterative cycling between model formulation and testing with observations. We also demonstrate the need to supplement traditional methods of model validation with techniques that provide information on how well the model captures the essential features of important atmospheric processes.

We illustrate the steps of model testing through an analysis of results from the simulation of an acid deposition episode with the comprehensive model ADOM (Acid Deposition and Oxidant Model). Model predictions of sulfate and nitrate in rain are compared with corresponding observations. In addition, the predictions are used to estimate event-averaged washout ratios. It is found that these washout ratios agree well with those estimated from recent observations. The geometric mean washout ratios for SO_2 (5×10^4) and SO_4 (6×10^5) are comparable to those used in semi-empirical long-range transport models.

Key word index: acid deposition model, long-range transport, washout ratios, model evaluation.

INTRODUCTION

Acid deposition is governed by a multitude of complex processes which include gas-phase chemistry, aqueous-phase chemistry, synoptic dynamics, micrometeorology, and cloud physics. The general consensus is that in order to take the steps required to alleviate the acid deposition problem, we need to understand the interactions between these processes. One of the ways of gaining this understanding is to use a simulation model that provides a mathematical description of the relevant processes. Such a model is constructed by assembling a set of submodels or modules, each of which corresponds to a different process (e.g., gas-phase chemistry). This model can be used to probe the complex interactions between the modules by conducting numerical experiments that would be impossible in the real world. In order to differentiate it from simpler semi-empirical models, such a model is referred to as a comprehensive model.

One of the major problems that face us in developing a comprehensive model is the fact that our understanding of the acid deposition system is far from complete. There is no guarantee that a combination of partially correct modules will have anything to do with reality. This is an important point because it is so easy to believe the results from a complex model with a rich repertoire of responses. While the a priori scientific content does lend credibility to the model, it cannot serve as a substitute for the verification of model predictions with observations. Comparison of model predictions with observations is a formidable task because of the enormous data requirements of a comprehensive model. Data sets that can be considered adequate are not available now, or are likely to be in the foreseeable future. This means that we have to be extremely

creative in devising methods to convince ourselves that the model is an adequate surrogate for reality.

This paper describes the formulation and testing of a comprehensive model for acid deposition. The model, called the Acid Deposition and Oxidant Model (ADOM), is being developed by ERT and MEP Co. (Canada) under the sponsorship of the Ontario Ministry of the Environment, Environment Canada, the German Umweltbundesamt, and the Electric Power Research Institute. A similar model, known as the Regional Acid Deposition Model (RADM), is being developed with funding from the U.S. EPA. The discussion that follows emphasizes the iterative relationship between model formulation and testing. These two aspects of model development do not follow each other in sequence as is commonly believed.

APPROACH TO THE DEVELOPMENT OF A COMPREHENSIVE MODEL

The overall objective of comprehensive modeling is to construct a numerical surrogate for the real system. Thus every attempt is made to incorporate all the relevant processes in as much detail as possible. However, our ability to do so is limited by three factors. First, we do not as yet have a complete understanding of all the relevant processes. Second, the inclusion of the detailed descriptions of all the processes (even if we understood them) is likely to strain the resources of the best available computers. The third reason for being less than comprehensive in the modeling is related to the need to test the model against observations. This testing is an iterative process in which discrepancies between model predictions and observations are used to improve the formulation of the model. This improvement is possible only if the major

cause-effect links in the model are reasonably transparent. Complexity in a model is clearly not compatible with this feature.

We see that the development of a comprehensive model has to be guided by two conflicting requirements. First, the model has to be complex enough to include the major processes of acid deposition. Second, it has to be simple enough to allow for reformulation and improvement as a result of testing against observations. It should be stressed that this need for "relative" simplicity acknowledges the fact that our understanding of acid deposition is far from complete. Therefore, we have to rely on observations made on the acid deposition system, as a whole, to calibrate the model, and thus be reasonably confident that the model is an adequate representation of reality. We are suggesting here that it is not practical or desirable to incorporate all our a priori knowledge of the processes of acid deposition into a comprehensive model.

The initial formulation of an acid deposition model will reflect the viewpoint of the group involved in its development. This subjectivity is likely to be less important as the model is tested against observations, and subsequently improved. However, as pointed out earlier, this process of model testing and reformulation is fraught with problems. Furthermore, there is little consensus on what constitutes adequate agreement between model predictions and observations, even if the data sets were available. Thus, this paper represents only a preliminary attempt to address a very difficult problem. We have just finished assembling a first version of ADOM, and we have begun to test it against data collected during the Oxidation and Scavenging Characteristics of April Rains (OSCAR) field study conducted in April 1981. The rationale for the initial formulation

of ADOM is best introduced with a brief description of the processes of acid deposition.

THE PROCESSES OF ACID DEPOSITION

The precursors of acid deposition are SO_2 and NO_x , most of which are emitted by anthropogenic sources. These gases are converted to sulfuric and nitric acids by a range of oxidants whose concentrations are controlled by a complex set of photochemical reactions. The major initiators of these reactions are hydrocarbons and NO_x , both of which are also produced by anthropogenic activities. The main gas-phase oxidant is the OH radical, which plays a major role in photochemistry. SO_2 dissolved in cloud (fog) droplets is also oxidized very efficiently by a variety of oxidants, the most important of these being H_2O_2 and O_3 , which are primarily produced in the gas phase. Alkaline agents such as ammonia and soil-dust derived carbonates also play a major role in aqueous-phase chemistry.

The other processes that govern acid deposition include transport by winds, and wet and dry deposition. Pollutants are dispersed in the horizontal and vertical directions by the three dimensional flow patterns of the atmosphere. Clouds play a major role in the fate of these pollutants. First, they serve as aqueous-phase reactors. Precipitation resulting from some of the clouds transfer the products of the aqueous-phase reactions to the ground as wet deposition. Clouds also induce air motions that result in vertical mixing of material through the depth of the troposphere. In addition to these effects, clouds also affect the solar radiation that controls photochemistry.

Pollutants that are transferred towards the ground can be removed from the atmosphere by a number of processes that are collectively referred to as dry deposition. The biological activity of the underlying surface and the solubility of the relevant gas in water are two of the many factors that affect dry deposition.

The next section describes how these processes are treated in ADOM.

THE MODULES OF ADOM

Like other Eulerian models, ADOM is based on the solution of the mass conservation equation for a pollutant:

$$\frac{\partial C}{\partial t} = -u_i \frac{\partial C}{\partial x_i} + \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial C}{\partial x_j} \right) + P - W - D \quad (1)$$

where C is the concentration, u_i is the velocity field, and K_{ij} is the eddy diffusivity, which is used to model transport by the unresolved velocity field. The term P represents chemistry, W denotes wet deposition, and D represents dry deposition. The first two terms on the right-hand side of the equation represent transport by atmospheric winds.

ADOM solves Equation 1 using a three-dimensional Eulerian grid with a horizontal spacing of approximately 100 km. The vertical grid, with 12 unevenly spaced levels between 0 and 10 km, is designed to resolve the higher concentration gradients in the boundary layer.

The relatively large horizontal spacing, which is imposed by computational constraints, can give rise to errors caused by the incorrect parameterization of processes that occur at subgrid scales. For example, ADOM mixes emitted pollutants instantaneously across the grid. In

addition to the artificial reduction of concentrations, this process might yield products of chemical reactions between pollutants that, in reality, do not come into contact with each other in that particular grid square. We have similar subgrid scale problems with processes such as cloud physics. It is difficult to quantify these errors during the formulation of the model. Until computational resources become far greater than they are now, we are forced to rely partially on the empirical approach of using the discrepancies between model predictions and observations to provide us with an indication of subgrid scale errors. This again points to the importance of the model testing phase in the development of a comprehensive model.

The terms in the differential equation yield a convenient division of the model into the following components: transport, gas-phase chemistry, wet scavenging, and dry deposition. A brief description of each module follows.

Transport

As its name implies, the transport module moves acidifying species and their precursors in a three-dimensional grid. The inputs to the module are horizontal and vertical winds and the eddy diffusivities that characterize transport by unresolved scales of motion. The core of the module is a sophisticated solver for the advection-diffusion equation. Although meteorological information controls the output, numerical errors can occur. Therefore, it is important to develop an accurate transport module that minimizes numerical diffusion.

The meteorological information is derived from a diagnostic module that combines information from the Canadian Meteorological Center (CMC) large-scale numerical weather prediction model with information from a high-resolution boundary layer model developed by the MEP Company of Toronto, Ontario (Scholtz et al., 1986). The CMC model essentially provides the upper boundary conditions for the boundary layer model.

It is noted that the meteorological module attempts to use model predictions to interpolate available observations. Because the techniques to do so are not always satisfactory, there are unavoidable inconsistencies in the meteorological fields. For example, precipitation might be predicted in a grid square in which there is no cloud cover. Such inconsistencies can be corrected by careful examination of the meteorological inputs. Although this might entail painstaking analysis, we prefer this approach to the alternative approach of generating meteorological fields from a dynamic primitive equation model.

Although the ADOM meteorological fields might have inconsistencies, they have the major virtue of being compatible with available observations. This allows us to avoid the prediction of meteorological fields in addition to the air quality fields, which are of primary concern to us.

Gas-phase chemistry

This important module simulates the complex chemistry of importance to acid deposition. It includes the photochemistry that yields the radical pool responsible for the conversion of emitted SO_2 and NO_x to H_2SO_4 and HNO_3 . The mechanism, which uses a "lumped molecule" approach,

consists of roughly 100 reactions among 50 species, of which 30 are transported by advection. It was obtained by condensing a detailed mechanism involving nearly 300 reactions among 100 species (Lurmann et al., 1986). The condensed mechanism produces results that compare well with smog chamber data and includes all the atmospheric reactions of importance to the acid deposition problem (Lurmann et al., 1986).

ADOM accounts for emissions of the primary reactants NO_x and SO_x , and reactive hydrocarbons. It is also necessary to specify emissions of NH_3 and soil dust, which play an important role in aqueous-phase chemistry. The gas-phase chemistry module is crucial to the performance of ADOM because it is responsible for the gas-phase conversion of SO_2 and NO_x to the corresponding acids. It also generates the primary aqueous-phase oxidants.

Wet scavenging

This module combines submodules for aqueous-phase chemistry and cloud physics. The submodule for the aqueous-phase chemistry consists of 25 reactions among 13 species. It includes the oxidation of S(IV) by O_2 , O_3 , and peroxides, and it incorporates a fairly complete treatment of mass transfer between the gas and aqueous phases.

A one-dimensional steady-state model that uses surface precipitation and other meteorological data simulates a stratiform cloud (Karamchandani et al., 1986). The "bulk water" technique is used for the microphysical formulation (Kessler, 1969). The cumulus cloud model is based on a parameterization derived from observations made in cumulus clouds (Warner, 1970). Both the cloud models are designed to serve three major functions

which are to 1) mix pollutants vertically, 2) act as aqueous-phase reactors and 3) scavenge pollutants.

Dry deposition

This module represents the dry-deposition velocity as the inverse of the sum of an atmospheric resistance, a deposition layer resistance, and a residual surface resistance. The atmospheric resistance is a function of the surface micrometeorology, and the deposition layer resistance depends upon the properties of the depositing species and surface friction velocity. Surface resistance is the most difficult to estimate because it is a function of many factors, including the biology of the deposition surface. For this reason, we are forced to rely largely on observations to provide typical values for this parameter.

APPROACH TO MODEL TESTING

We see that ADOM provides a reasonably complete description of the acid deposition system. However, as mentioned earlier, it is neither desirable nor practical to include all the details of our current understanding of the relevant processes. For example, we have not made a vigorous attempt to incorporate currently available cloud models that include detailed microphysics. In order to neglect such details we have to make the assumption that the acid deposition system as a whole responds to the dominant aspects of the individual processes. It is further implied that the current parameterizations capture the essential characteristics of these processes. However, we expect the comparison of

model predictions with observations to lead to the modification of some of the modules of the model. As mentioned earlier, this interaction between model testing and reformulation is possible only if the model is reasonably transparent to the analyst.

Because there are practical limits to satisfying the input requirements of ADOM, direct comparison of model predictions with corresponding observations will always yield results that are difficult to interpret. This problem is exacerbated by our incomplete understanding of the governing processes. In light of this, we have to supplement traditional methods of model testing with new techniques that explicitly account for the nature of comprehensive models. This paper introduces a technique that we have found useful in testing ADOM.

This component of model testing attempts to find out whether the overall responses of the model are similar to those of the real acid deposition system. It acknowledges the fact that inevitable errors in model inputs will complicate the direct comparison of observations with predictions from even a "perfect" model. Therefore, it is useful to supplement this direct comparison with the use of semi-empirical models to establish the connection between the behavior of the comprehensive model and that of the real system.

A semi-empirical model derives most of its credibility by being able to describe observations, although it is incapable of providing detailed explanations for the cause-effect relationships of the acid deposition system. Most existing long-range transport models can be classified as semi-empirical, examples of which are provided by those formulated by Eliassen and Saltbones (1983), Fisher (1978), and Venkatram and Pleim (1985). In these models, processes such as chemistry and scavenging are

represented by parameters whose values are essentially derived by fitting model predictions to observations. One of the attractive features of these models is their ability to provide concise descriptions of the acid deposition system. We can take advantage of this feature by noticing that these descriptions refer to the overall behavior of the acid deposition system rather than a particular event. What this means is that we can use semi-empirical models to describe the responses of the comprehensive model without worrying too much about errors in the model inputs corresponding to any particular situation.

The basic idea is that if the responses of the model are similar to those of reality, the same semi-empirical model should apply to both the model and the real acid deposition system. In other words, the values of the model parameters obtained by fitting the semi-empirical model to predictions from the comprehensive model should be similar to those from the real system if the comprehensive model is an adequate surrogate for reality. This testing method treats the predictions from the comprehensive model as synthetic observations. Figure 1 illustrates the basic concepts discussed here.

In the next section, we illustrate the preliminary application of our ideas on testing a comprehensive model.

MODEL RESULTS

ADOM has been applied to an acid deposition episode corresponding to Event 2 (April 11 to 15, 1981) in the OSCAR field study. The study, which has been described in detail elsewhere (Easter et al., 1984), was conducted during April 1981 to investigate wet removal by cyclonic storms.

One of the components of the field study was an intermediate-density precipitation chemistry network, consisting of 37 stations in the eastern U.S. and Canada at a spatial resolution of 100 to 200 km.

During the early part of Event 2, precipitation occurred largely as showers and thunderstorms. However, the eastern portion of the intermediate-density network experienced mostly steady, warm front-type rain. A few stations in the network received little or no rainfall and/or had significant amounts of bad or missing data. The bulk of the precipitation occurred on the 13th and 14th of April. Western stations in the intermediate-density network were alerted to sample at 1200 GMT on April 13 while the rest of the network was alerted at 1800 GMT on the same day. However, a few stations also sampled on April 12 without receiving a final alert. Figure 2 shows the cumulative precipitation field used in model simulations for the five-day event (April 11 to 15). The highest precipitation amounts (>40 mm) are accumulated in an approximately east-west band extending from southern Iowa and northern Missouri to southeastern Pennsylvania and Maryland. Most of the high precipitation amounts are associated with convective activity. Portions of the northeast and the rest of the east experienced mostly warm front-type rain, with cumulative precipitation amounts less than 40 mm. The southern, southeastern, and northwestern portions of the grid were relatively dry, receiving less than 10 mm of cumulative precipitation.

A base case simulation of the five-day episode was carried out using relatively clean initial and boundary conditions. The first two days of the simulation (April 10 and April 11) served as a "warm-up" period to allow the model to flush out the prescribed initial conditions and achieve a state that is dominated by the gridded emissions and transport. Thus,

by the time a significant amount of precipitation is experienced in the domain (April 13), pollutant concentrations have reached levels that are essentially independent of the initial conditions.

The model predicts hourly concentration and deposition fields of the major pollutants. Although this information is useful for diagnostic purposes, it is more convenient to present model results in the form of daily or event averages. Figure 3 shows predicted 24-hour average gas-phase SO_4 concentrations for April 14. Pockets of high concentrations of SO_4 (from 8 to $10 \mu\text{g}/\text{m}^3$) are predicted in southern Mississippi and the Carolinas. These high concentrations can be attributed to three factors: a) large SO_2 emissions (up to 1,000 metric tons per day) in Louisiana, Mississippi and South Carolina, slightly upwind of the high concentrations; b) light winds in the south (less than 2.5 m/s) associated with a high over Georgia; and c) little or no precipitation in the southern region to scavenge the sulfate. Lower concentrations (less than $6 \mu\text{g}/\text{m}^3$) that are predicted downwind of major SO_2 sources in Ohio, Detroit, and Chicago reflect the effects of wet scavenging.

The predicted cumulative wet sulfur deposition field for the five-day event is shown in Figure 4. The maximum deposition ($>0.70 \text{ Kg}/\text{Ha}$ in 120 hours) is predicted in eastern Ohio, and western and southern Pennsylvania. Slightly lower deposition amounts (from 0.25 to $0.55 \text{ Kg}/\text{Ha}$) are predicted in other portions of Ohio and Pennsylvania, and in portions of Illinois, Indiana, West Virginia, Virginia and New York.

For a given hour, the model treats grid cells dominated by small-scale precipitation with the cumulus cloud module, while grid cells dominated by large-scale precipitation are treated with the stratus cloud module. However, the distinction between the two cases is not as

clear-cut when event averages are calculated, since a grid cell can be treated with either module at different hours during an event. Nevertheless, it is useful to compare the performance of the two modules on an individual basis, particularly since one module treats cloud microphysics and is fairly complex, while the other module is relatively simple.

Figure 5 compares observed and predicted wet sulfate concentrations, using data from the intermediate-density network. Since event durations vary from one site to another, precipitation weighted average concentrations are determined using the actual duration of the event at each sampling site. The agreement between predictions and observations is reasonably good for a majority of the cells with 90% of the concentrations predicted within a factor of two. On the surface, it appears that the cumulus cloud module tends to underpredict sulfate concentrations in precipitation. However, a sensitivity study which used the cumulus cloud module in grid cells previously treated with the stratus cloud module yielded similar results. Thus, the overestimates do not appear to be related to any bias in the cumulus module. This sensitivity study also indicates that it might be possible to simplify the stratus cloud module without degradation of model predictions. A possible reason for the apparent bias may be a mismatch between observed and model-used precipitation amounts. Figure 6 shows that most of the underestimates of sulfate in precipitation can be attributed to observed precipitation amounts being lower than those used in the model.

Figure 7 compares event-averaged nitrate concentrations in precipitation. The agreement between observations and predictions is not as good as it is for sulfate, although a majority (60%) of the concentrations are

predicted within a factor of two. There also appears to be a tendency toward overprediction. Underestimates with the cumulus cloud model are again associated with discrepancies between model-used and observed precipitation amounts.

Although there is reason to be encouraged by the performance of the model against observations, it is important to supplement direct comparisons of model predictions and observations with techniques that can tell us whether model results are consistent with the inputs provided to it. This is particularly important for comprehensive models such as ADOM, which consist of several submodules for the representation of different atmospheric processes. Insight into model performance can be obtained by other traditional methods. For example, sensitivity studies can be performed to test the response of the model and its individual submodules to variations in input data. Model results can be analyzed carefully to check for anomalies. Such techniques are useful (and necessary) to reassure ourselves that the model is not doing something terribly wrong, even if the model predictions appear reasonable.

Next, we illustrate the use of a semi-empirical model to test the performance of ADOM. Most long-range transport models represent wet scavenging of pollutants by using parameters such as washout ratios and scavenging coefficients. The parameters are tuned to provide the best fit between model predictions and observations. The washout ratio is defined as the ratio of the concentration of pollutant in precipitation to its concentration in air at the surface. Typical values for washout ratios used in semi-empirical models are on the order of 5×10^4 for SO_2 and 10^6 for SO_4 (e.g., Eliassen and Saltbones, 1983). Measurements based on the definition of the washout ratio have similar magnitudes (Misra et al.,

1985). The washout ratio thus represents a semi-empirical model for the scavenging process. It is therefore useful to find out whether this model also describes the output from ADOM.

We estimate the washout ratios of SO_2 and SO_4 by separating the contributions of in-cloud oxidation and scavenging of pre-existing sulfate to sulfur in precipitation. Figure 8 presents boxplots of estimated washout ratios using model predictions at sites in the OSCAR intermediate density network. These boxplots show the range of washout ratios, the median, the lower and upper quartiles, and probable outliers. The washout ratios exhibit a fair amount of variability with a range spanning an order of magnitude for SO_2 and SO_4 and almost two orders of magnitude for NO_3 and NH_3 . They are also found to be log-normally distributed. These characteristics are in agreement with recent estimates of washout ratios from observations (Misra et al., 1985). The geometric mean SO_2 washout ratio is 5×10^4 , while the geometric mean SO_4 washout ratio is 6×10^5 . These are comparable to washout ratios used in semi-empirical models (Eliassen and Saltbones, 1983), which have generally been applied to estimate the long-range transport and deposition of sulfur species only. The geometric mean NO_3 and NH_3 washout ratios (which include pollutant in both the particulate and gaseous state) are 5×10^5 and 2×10^5 , respectively. These results show that the modeling of wet scavenging in ADOM is not inconsistent with the empirical descriptions of the process. We do realize that this comparison represents only a rudimentary application of our ideas on the use of semi-empirical models to test ADOM.

SUMMARY

Results from a base case simulation of an acid deposition episode (OSCAR II, 1981) with a comprehensive regional-scale model show that, for the most part, the model predicts expected features of the acid deposition system. Event-averaged concentrations of sulfate in rain are within a factor of two of the observations for 90 percent of the data. The corresponding number for nitrate predictions is 60 percent. Although such comparisons of model predictions and observations provide a useful measure of model performance, they are complicated by inevitable errors in model inputs and evaluation data sets. Supplemental techniques are required to test comprehensive models. As an illustration of such techniques, washout ratios are estimated from predicted concentration and deposition fields to see how they compare with those traditionally used in semi-empirical long-range transport models, and with those estimated from observations. The estimated washout ratios exhibit characteristics that are similar to those estimated from recent observations, while the geometric mean washout ratios for SO_2 and SO_4 are comparable to those used in semi-empirical models.

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LIST OF FIGURES

- Figure 1. Steps involved in screening of the comprehensive model with an empirical model.
- Figure 2. Cumulative precipitation (mm) for OSCAR 2 (April 11-15, 1981).
- Figure 3. Predicted 24-hour (April 14, 1981) average surface concentrations ($\mu\text{g}/\text{m}^3$).
- Figure 4. Predicted cumulative wet sulfur deposition (Kg/Ha) for April 11-15, 1981.
- Figure 5. Event-averaged, precipitation-weighted wet sulfate concentrations.
- Figure 6. Observed to predicted wet sulfate concentration ratios versus observed to model-used precipitation ratios.
- Figure 7. Event-averaged, precipitation-weighted wet nitrate concentrations.
- Figure 8. Boxplots of event-averaged estimated washout ratios.

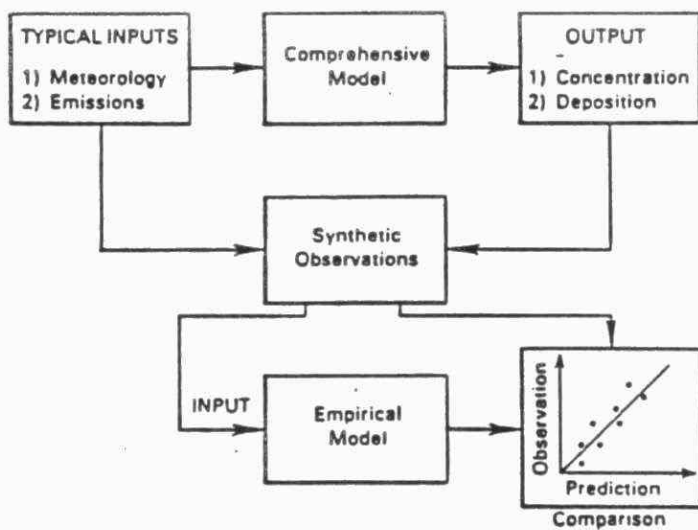


Figure 1

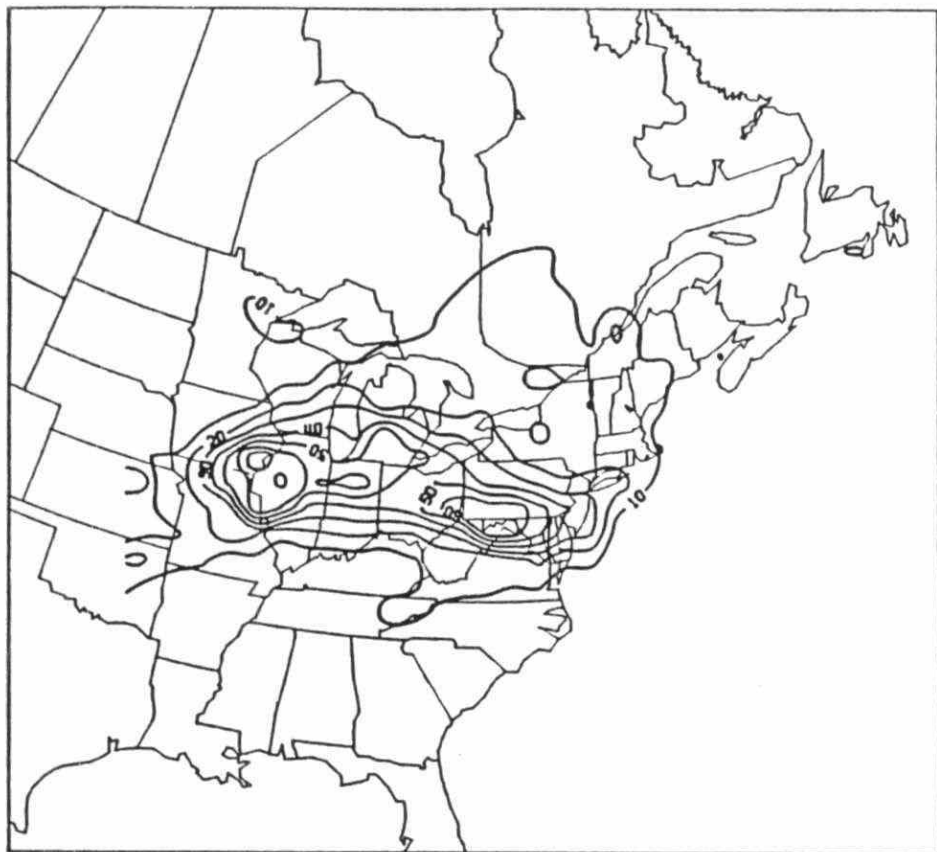


Figure 2

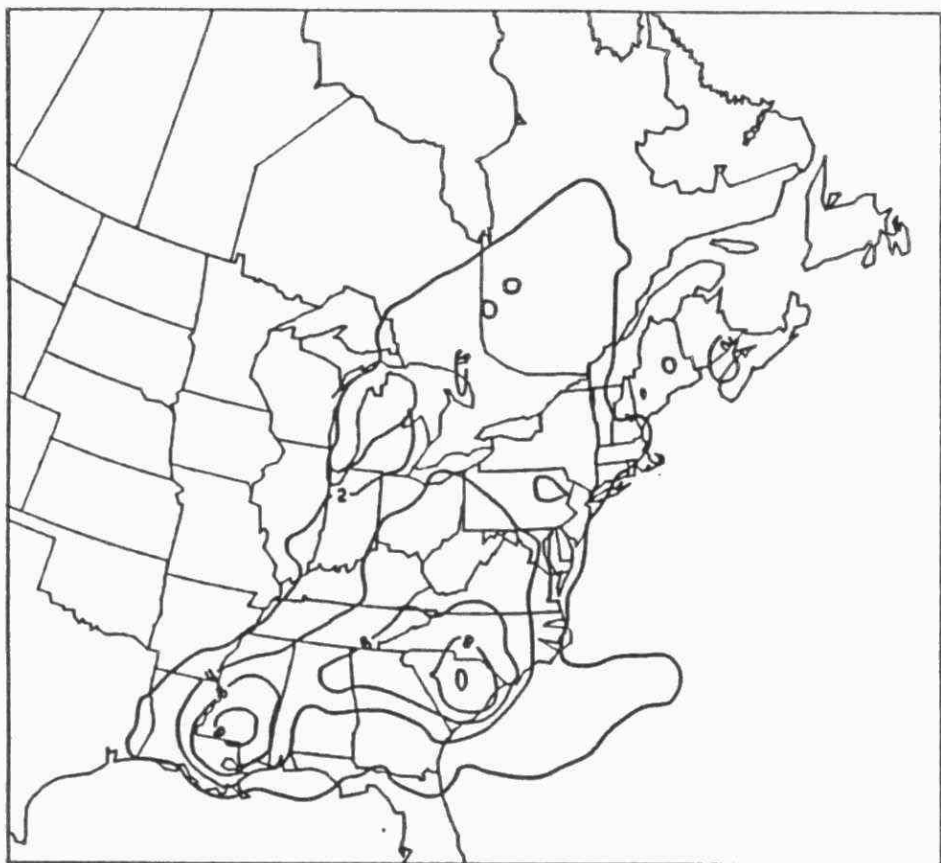


Figure 3

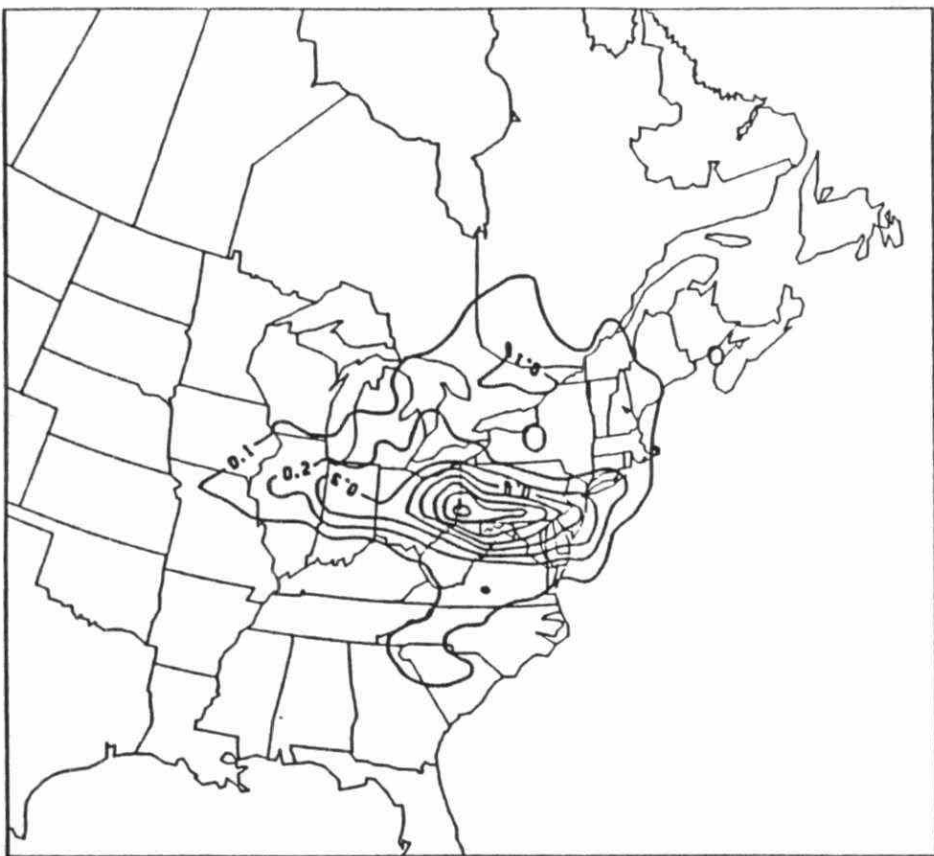


Figure 4

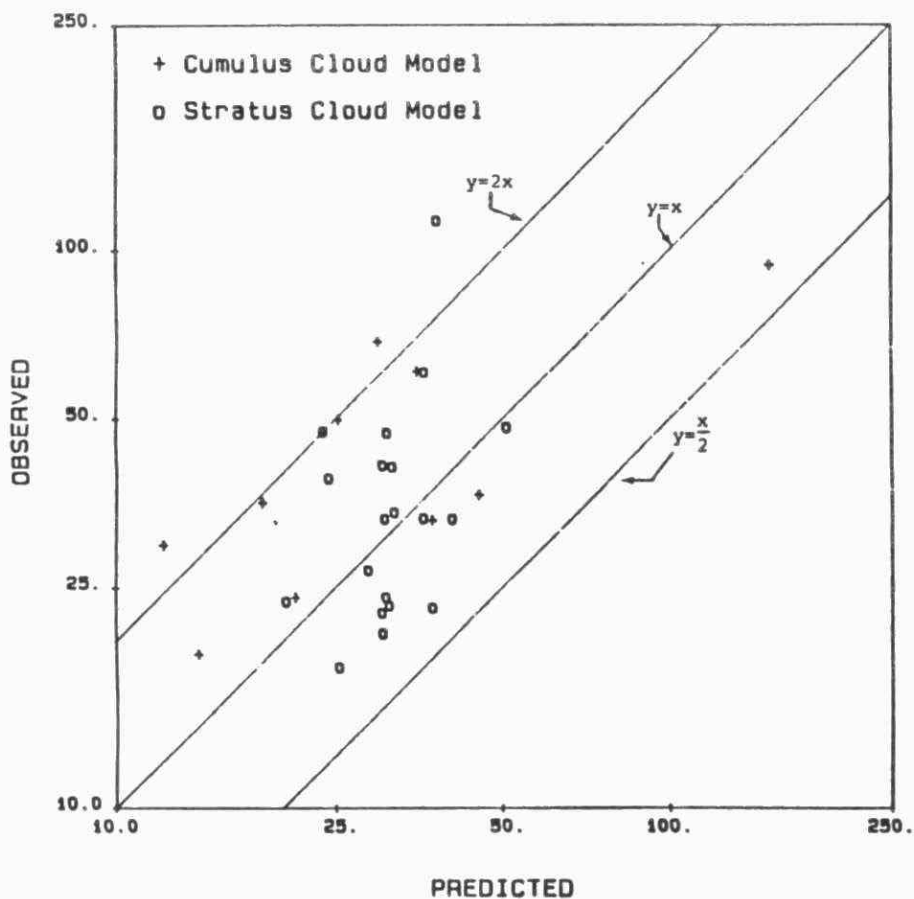


Figure 5

OBSERVED CONCENTRATION/PREDICTED CONCENTRATION

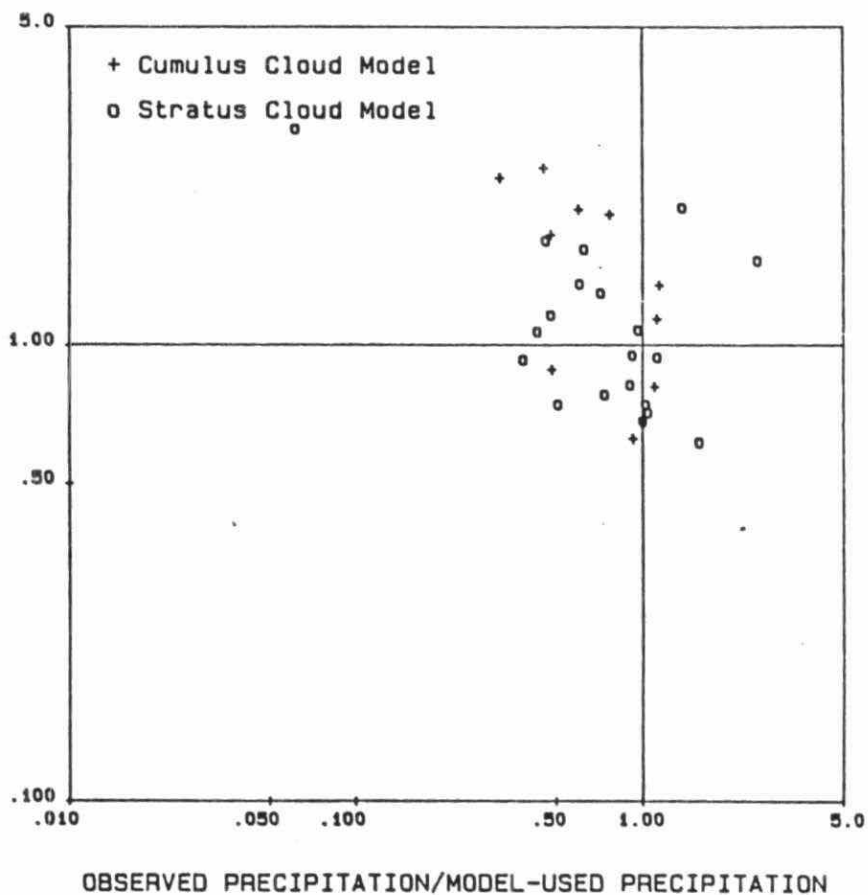


Figure 6

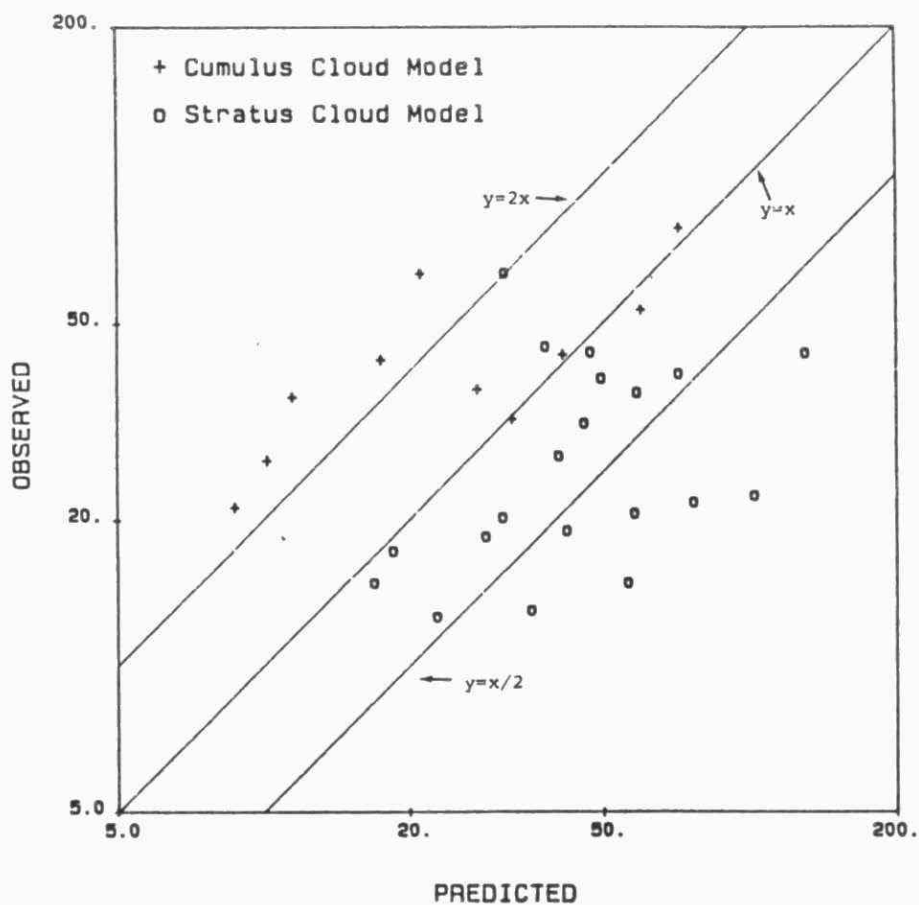
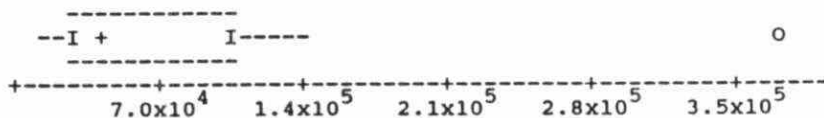
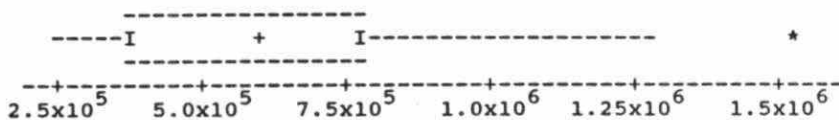


Figure 7

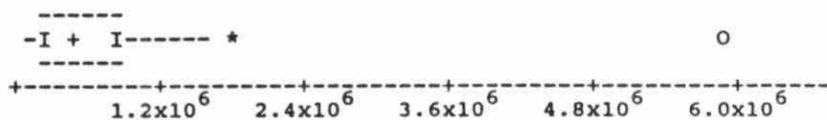
1. SO_2



2. SO_4



3. NO_3



4. NH_3

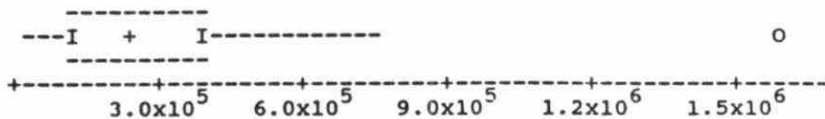


Figure 8



An Eulerian Model of Long Range Transport of Air Pollutants and Acid Rain

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1. Introduction.

An Eulerian long-range transport model is being developed at the University of Toronto for the purpose of air pollutant transport and acid rain studies. The model consists of the following components:

- (1) An Eulerian atmospheric dynamic prediction model,
 - (2) models of cloud dynamical and microphysical processes,
 - (3) a model of cloud chemical processes,
- and (4) a model of gas phase chemistry.

The development of the first three components of the model is now complete and ready for research applications; a gas phase chemistry module will be developed and implemented into the model in the coming year. We report in this paper the model structure, the physical and chemical processes described by the model, and some preliminary results from an OSCAR 4 (Oxidizing and Scavenging Characteristics of April Rain experiment - period 4) simulation.

2. The atmospheric dynamic prediction model.

The dynamic component of the model is based on the hydrostatic, primitive equations written in the σ -coordinate system. It describes the dynamics of air flow in the atmosphere. Figure 1 shows the model domain and the numerical grid. There are 52 x 52 grid points over the domain, with a horizontal resolution of 127 km, and ten layers in the vertical, with the following values of σ at the boundaries between the layers.

$\sigma_1 = 1$	$\sigma_6 = 0.400$
$\sigma_2 = 0.95$	$\sigma_7 = 0.325$
$\sigma_3 = 0.90$	$\sigma_8 = 0.250$
$\sigma_4 = 0.80$	$\sigma_9 = 0.175$
$\sigma_5 = 0.60$	$\sigma_{10} = 0.100$
	$\sigma_{11} = 0.000$

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** Ontario Hydro

The model also incorporates full topography. Figure 2 shows contours of ground surface height above sea level in metres. The feature in the upper right-hand corner is Greenland.

In addition to the basic dynamics, a number of physical and chemical processes are also included in the model; they are:

(1) Stratiform clouds

Stratiform clouds are described in the model through detailed calculations of microphysical processes which will be discussed in section 3.

(2) Cumulus clouds

In the present version of the model, cumulus clouds are parameterized according to the Kuo scheme (Kuo, 1965): They are not resolved explicitly.

(3) Cloud chemistry

Chemical reactions taking place in stratiform clouds involving SO_2 and NO_x calculated using the cloud chemistry model described in section 4.

(4) Dry deposition

Dry deposition of chemical species SO_2 , NO and NO_2 are described in the model interims of dry deposition velocities. The dry deposition velocity field used for SO_2 was derived from published information (Voldner et al., 1986); it is shown in Figure 3. At present, the same dry deposition velocity field used is also used for NO and NO_2 .

(5) Emissions.

The emission field for SO_2 and NO_x used in this project are shown in Figures 4 and 5, respectively. They were derived from data assembled for the Ontario Ministry of the Environment (Northeastern North America) and published Provincial and State totals (the rest of the Continent). In the case of NO_x emission, the assumption was made that 17% of emitted NO_x is in the form of NO and 83% in the form of NO_2 .

3. Cloud Microphysics

The cloud microphysics model describes the physical changes water undergoes in clouds. This includes changes of state (e.g., condensation, freezing, and melting) as well as interactions among the condensed water forms (e.g., accretion and riming).

In addition to water vapour, V, five species of hydrometeors (condensed water forms) are considered - cloud water, C; cloud ice, I; rain, R; snow, S; and graupel or hail, G (see Figure 6). Cloud droplets and ice crystals are assumed to be of uniform size and to follow the air motion,

while precipitation particles are assumed to have an exponential size distribution and to fall at the velocity corresponding to their mass weighted mean diameters. The limit between cloud droplets and raindrop is taken to be 200 μm diameter; that between ice crystal and either snow or graupel, 400 μm diameter of the circumscribed sphere, or alternatively a mass of 5×10^{-9} kg.

The interactions between hydrometeors considered in the model are illustrated in Figure 6. Each interaction represents a source (or sink) for the amount of hydrometeors involved. These interactions are explained in Table 1.

Following the table, each interaction is identified by a number and two letters; for instance, 4CR indicate "accretion of cloud droplets by raindrops"; the corresponding source term is $S(4CR)$ (a sink for r_c and a source for r_R).

Several further remarks can be made regarding the table. The vapour deposition and evaporation terms can be treated generally by the kinetic formula based on the diffusion around the particle. The use of this expression entails the need for very strong simplifications, particularly for ice crystals and snow, and with it, a large degree of uncertainty. However, when dealing with ascending air in a liquid cloud, where vapour saturation with respect to water can be assumed, the rate of condensation can be safely and accurately calculated from thermodynamics (wet adiabats); and similarly for ice clouds, with vapour saturation with respect to ice. Thus the term 1VC (vapour deposition in water saturated cloud) is calculated differently from 1CV (evaporation of cloud droplets). For ice crystals 1VI is calculated thermodynamically in a saturated ice cloud and kinetically otherwise. 1IV, as well as 1SV and 1GV are between brackets in the table because these terms will use the same formula (except for the sign), as 1VI, 1VS and 1VG, respectively.

The "warm rain" process starts with the triggering term 3CR ("autoconversion") and continues with growth terms, mainly 4CR (accretion of cloud droplets). The triggering term for the Bergeron-Findeisen process is 2CI (freezing of cloud droplets on ice nuclei), to be followed by 1VI (vapour deposition), 5IS or 5IG (transformation into snow or graupel by growth), 6CS or 6CG (riming), etc.

4. Cloud chemistry.

Cloud chemistry deals with the exchange of chemicals between the gas and liquid phases, with their transfers between hydrometeors and with the chemical reactions that take place in the cloud (i.e., in the liquid phase and the interstitial air). A first exchange of chemicals can take place when the cloud droplets first form, through the mechanism of nucleation. Chemical compounds are introduced into the cloud as gases contained in the air (SO_2 , NO , NO_2 , H_2O_2 , O_3 , HNO_3 , NH_3) or as solid or liquid components of the aerosol (including acid or basic species), whose particles (or a large mass fraction of them) act as cloud condensation nuclei. Once the cloud droplets have formed, the interphase exchange of chemicals will continue through the

mechanism of diffusion. However, under conditions of very small droplet size or sparingly soluble gases, equilibrium between the gas and liquid phases can usually be assumed, thus simplifying the computations enormously.

The reactions included in the model are:

- a) Oxidation of SO_2 in the liquid phase by H_2O_2 dissolved from the air;
- b) Oxidation of SO_2 in the liquid phase by O_2 dissolved from the air;
- c) Oxidation of SO_2 in the liquid phase by radicals OH and HO_2 scavenged from the air;
- d) Oxidation of NO by OH in the gaseous phase, with subsequent dissolution of the HNO_2 formed; and,
- e) Oxidation of NO by OH in the gaseous phase, with subsequent dissolution of the HNO_2 formed.

The liquid phase catalytic oxidation of SO_2 by dissolved O_2 can be important near urban areas where the concentrations of Mn and Fe are elevated. This and other reactions can easily be incorporated in the model, at a later date.

Listings of the dissociation constants, Henry's law coefficients, reaction rates and reaction rate constants for all the species and reactions in the cloud chemistry model are given in Tables 2 and 3.

5. An OSCAR 4 simulation.

A simulation was made using the Eulerian model for a 12-hour period of OSCAR 4. The simulation began at 12:00 GMT, April 23, and ended at 00:00 GMT, April 24, 1981. Figure 7 shows the surface weather map, and 500 mb height contours at the beginning of the simulation period.

The weather situation was dominated by a 992 mb low pressure center over Lake Michigan and a high pressure system to the west over the Rockies and high plain states. A front was analyzed extending from the lower Great Lakes through Illinois to Texas. A short wave pattern centered at Arkansas was clearly identifiable on the front.

In the north, there were two low pressure systems: one off the east coast of Nova Scotia, another to the west of British Columbia over the Gulf of Alaska. These systems all have clear signatures on the 500 mb map. Comparing with weather maps 24 hours earlier, the two low pressure systems over Lake Michigan and off the Canadian east coast had intensified substantially over the 24-hour period while the other two maintained their strength at about the same level.

Figures 8, 9 and 10 show the wind, temperature in (T-300) K, and water vapour mixing ratio at the $\sigma = 0.97$ level at the beginning of the simulation period. Note that in the wind field there was a region of strong confluence extending from over Ohio southwestward to Texas. There was also a region of deformation flow centered at the eastern end of Lake Ontario. The temperature field shows a baroclinic belt located in Canada looping around Hudson's Bay.

These observed and analyzed meteorological fields were used as the initial conditions for the model. The simple assumption was made that there were no cloud fields at the initial time.

Figures 11 and 12 show the 12-hour simulation results of temperature and water vapour mixing ratio fields at 00:00 GMT, April 24, 1981. Over the regions of confluence and deformation, two fronts developed, one in the NE-SW direction stretching from Illinois to Texas, another in the NW-SE direction over the Great Lakes. There were strong gradients in temperature and humidity across these fronts.

There was considerable convective instability along the front over the midwest and southwest U.S., and in the low pressure system over the Gulf of Alaska. Since cumulus clouds are parameterized using Kuo's scheme, they are not computed explicitly in the model using our cloud microphysics model. Figure 13 shows the 12-hour accumulated precipitation produced by these convective clouds. The peak value along the front is 0.26 cm of rain; it accounts for only about 50% of the observed precipitation amount over that area. Kuo's scheme underestimated the amount of convective activity in this case.

Figure 14 shows the 12-hour accumulated precipitation produced by stratiform clouds. These clouds were calculated and predicted explicitly using the cloud microphysics model. There were considerable amounts of stratiform clouds in all four low pressure systems, and along the front over the Great Lakes. The predicted peak value along this front was 0.63 cm while the observed value was about 0.5 cm. This good agreement, however, should be treated with caution. As the initial cloud fields were assumed to be zero in the model, the predicted 12-hour precipitation amount is expected to be smaller than that observed.

For lack of better information, the initial fields of SO_2 , NO and NO_2 were assumed equal to 6 hours of accumulation of source emissions and distribution in the lowest three layers of the model in the 5:3:2 ratio. Uniform distributions of O_3 , H_2O_2 and CO_2 were assumed through the model volume at the initial time with values of 40 ppb, 2 ppb, and 340 ppm, respectively.

The initial fields of SO_2 and NO_2 at the $\sigma = 0.975$ level are given in Figures 15 and 16, respectively. They reflect the distributions of the source emission fields. The SO_2 concentrations are highest over the Ohio Valley, while the NO_2 concentrations have three separate maximum regions, over the Ohio Valley, Texas, and the State of California.

The next set of figures shows the 12-hour simulation results at the $\sigma = 0.925$ level. The distribution of SO_2 and NO_2 (in both air and cloudwater) are shown in Figures 17 and 18, respectively. The effect of advection is visible in both fields; the distributions begin to resemble the shape of the frontal systems over the Great Lakes and cross the Midwest and Southwest United States. The peak value of the SO_2 fields is 24.4×10^{-9} in mass mixing ratio, while that of the NO_2 field is 1.82×10^{-9} in volume mixing ratio.

Figure 19 shows the distribution of SO_4^{2-} in cloudwater. The SO_4^{2-} concentration carried in cloudwater is highest in the frontal system over the Great Lakes; the peak concentration there is 1.29×10^{-10} kmol per kg of air. In other cloud regions the values are only of the order of 2×10^{-12} kmol/kg.

Figures 20 through 22 show the distributions of S(IV) , SO_4^{2-} , and NO_3^- carried in rain water. Significant amounts of these species exist only in the frontal system over the Great Lakes. The peak values S(IV) , SO_4^{2-} , and NO_3^- are 2.1×10^{-13} , 6.8×10^{-12} , and 5.93×10^{-13} , respectively; all are in units of kmol per kg of air.

6. Conclusions.

We reported in this paper the development and some test results of a Eulerian long-range transport model being developed at the University of Toronto. The results of the test simulation appear reasonable within the context of microphysics and chemistry formulations. Because of the modular structure of the model, individual components of the model, such as the cloud microphysics and chemistry models are transportable and can be easily used in other types of Eulerian transport models as well. At the same time, because of its modular structure, the model is not yet optimized in terms of computing efficiency. For example, most parts of the microphysics and chemistry programs, as they stand, are not vectorized, which makes them rather inefficient to run on a vector computer.

As well, there are a number of areas in microphysics, chemistry, and their implementation on the Eulerian model which need improvement in the future. They are:

(1) Cumulus representation.

In the test simulations, microphysics and chemistry were computed explicitly only for stratiform clouds. Cumulus clouds were parameterized using Kuo's scheme; chemistry and microphysics in these clouds were completely ignored.

(2) Gas phase chemistry.

No gas phase chemistry was considered in the test simulations. This is a major defect of the Eulerian model. Gas phase chemistry is necessary if realistic comparison is to be made between simulation results and observations, especially for long period simulations.

(3) Boundary layer physics.

Only a simple turbulence diffusion based on the K-theory is used in the model to represent boundary layer processes. But boundary layer processes are very important to the physics and dynamics of the atmosphere, as well as to the transport and deposition of air pollutants. A better boundary layer physics model is needed.

(4) 24-48 hour simulations.

In our test simulation, a zero cloud field was assumed as the initial condition, and it required more than 6 hours before cloud fields were established in the model simulation. Unless cloud fields can be properly initialized somehow, realistic simulations of cloud fields can be expected only after 12 hours of integration. Simulations for longer periods of time are highly recommended for future studies.

(5) Model verification.

No attempts have been made yet to verify the model results using observations. This task should have high priority in future studies, especially for 24- or 48-hour simulations of cases such as OSCAR 4.

At the same time, the general problem of model verification should be examined carefully. What constitutes a good agreement between model results and observations? For a model of given resolution, how much data are needed to verify the model? How much data are needed to initialize the model in order to achieve a good simulation? There are as yet no clear answers to these questions.

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Table 1 - Interactions Between Hydrometeors

Species	Symbol	Evaporation- -Condensation	Melting- -Freezing	Coalescence	Accretion	Growth	Riming
		1	2	3	4	5	6
Water vapour	V	CV EV (IV) (SV) (GC)	-	-	-	-	-
Cloud droplets	C	VC	IC	-	-	-	-
Raindrops	R	VR	SR	CR GR	CR -	-	-
Ice crystals	I	VI	CI -	-	-	-	-
Snow	S	VS	-	-	IS	IS	CS
Graupel or hail	G	VG	RG	-	-	IG	CG RG

Table 2 - Dissociation Constants and Henry Coefficients

K_1 = dissociation constant; H_1 = Henry coefficient, in M atm⁻¹

Formula	Reference
$K_a = 1.2233 \times 10^6 e^{-\left[\frac{10294.83}{T} + 0.039282 T\right]}$	Beutier and Renon, 1978
$\log_{10} K_{SO_2,1} = \frac{853}{T} - 4.74$	Maahs, 1982
$\log_{10} K_{SO_2,2} = \frac{621.9}{T} - 9.278$	"
$\log_{10} H_{SO_2} = \frac{1376.1}{T} - 4.521$	"
$\ln K_{CO_2} = 2767.92 - \frac{80063.5}{T} - 478.653 \ln T + 0.714984 T$	Edwards et al., 1975
$\ln H_{CO_2} = -1082.37 + \frac{34417.2}{T} + 182.28 \ln T - 0.25159 T$	"
$H_{H_2O_2} = 4.67 \times 10^{-6} e^{6990/T}$	Martin and Damschen, 1981
$H_{O_2} = 5 \times 10^{-6} e^{2304/T}$	Kosak-Channing and Helz, 1983

Table 3 - Reaction Rates and Rate Constants

Reaction formulas		Reference
$v_{H_2O_2} = k_{H_2O_2} \frac{[HSO_3^-][H_2O_2][H^+]}{0.1 + [H^+]}$	$M s^{-1}$	Martin and Damschen, 1981
$k_{H_2O_2} = 9.42 \times 10^{11} e^{-3608/T}$	$M^{-1} s^{-1}$	Penkett et al., 1979
$v_{O_2} = k_{O_2} \left(1 + \frac{2.39 \times 10^{-11}}{[H^+]} \right) [O_2][S(IV)]$	$M s^{-1}$	Maahs, 1983
$k_{O_2} = 6.75 \times 10^9 e^{-2887/T}$	$M^{-1} s^{-1}$	Penkett et al., 1979
$v_{NO_2} = k_{NO_2} POHPNO_2$	$atm s^{-1}$	Atkinson and Lloyd, 1984
$k_{NO_2} = 4.2 \times 10^8$	$atm^{-1} s^{-1}$	"
$v_{NO} = k_{NO} POHPNO$	$atm s^{-1}$	"
$k_{NO} = 2.5 \times 10^8$ (pressures in atm)	$atm^{-1} s^{-1}$	"
$s_{OH} = 4 \times 10^{-10}$	$kmol m^{-2} s^{-1}$	Chameides and Davis, 1982
$s_{HO_2} = 2 \times 10^{-9}$	$kmol m^{-2} s^{-1}$	"

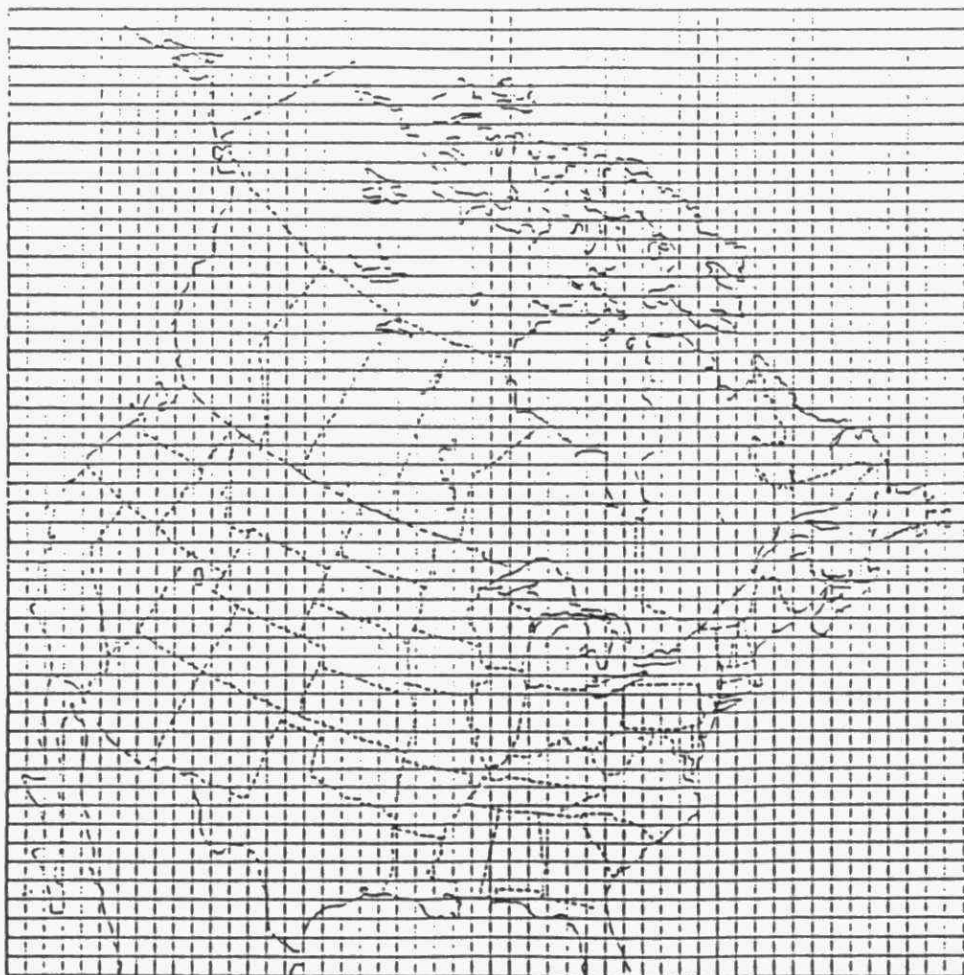
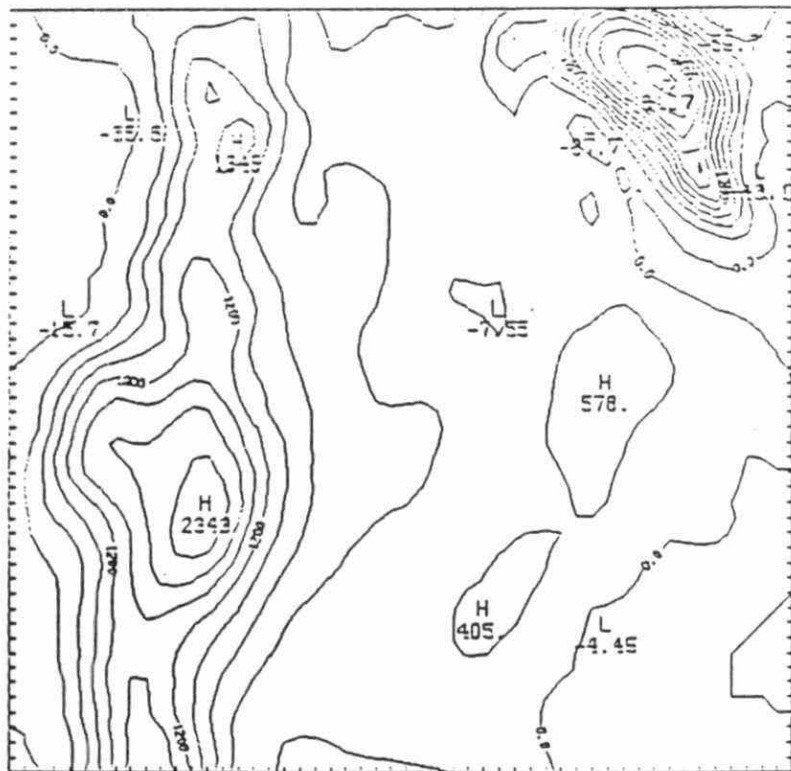


Figure 1. CMC Grid System Used in the Eulerian Model.
There are 52 x 52 Grid Points in the Horizontal,
with Horizontal Resolution of 127 km.



CONTOUR FROM 0.00000E+00 TO 3000.0 CONTOUR INTERVAL OF 300.00 P1(2,3)= 21.527

Figure 2. Contour of Ground Surface Height Above Sea Level in Metres.

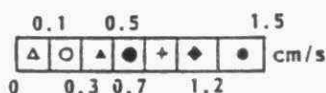
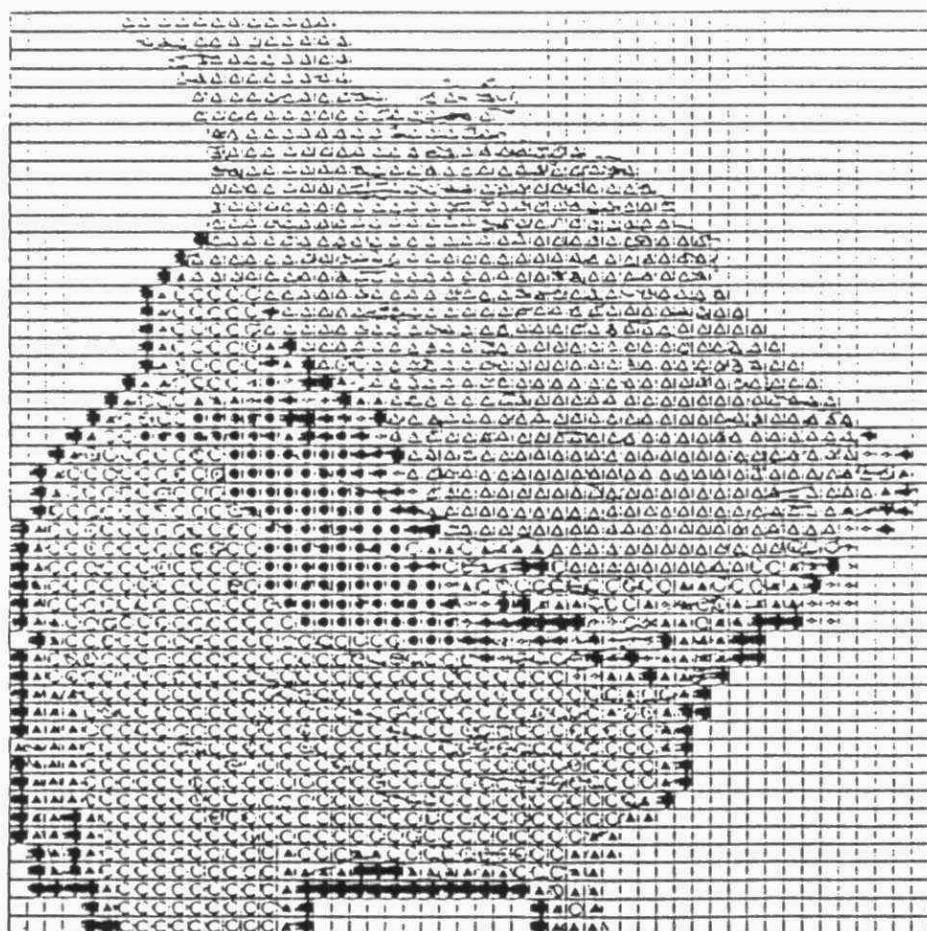
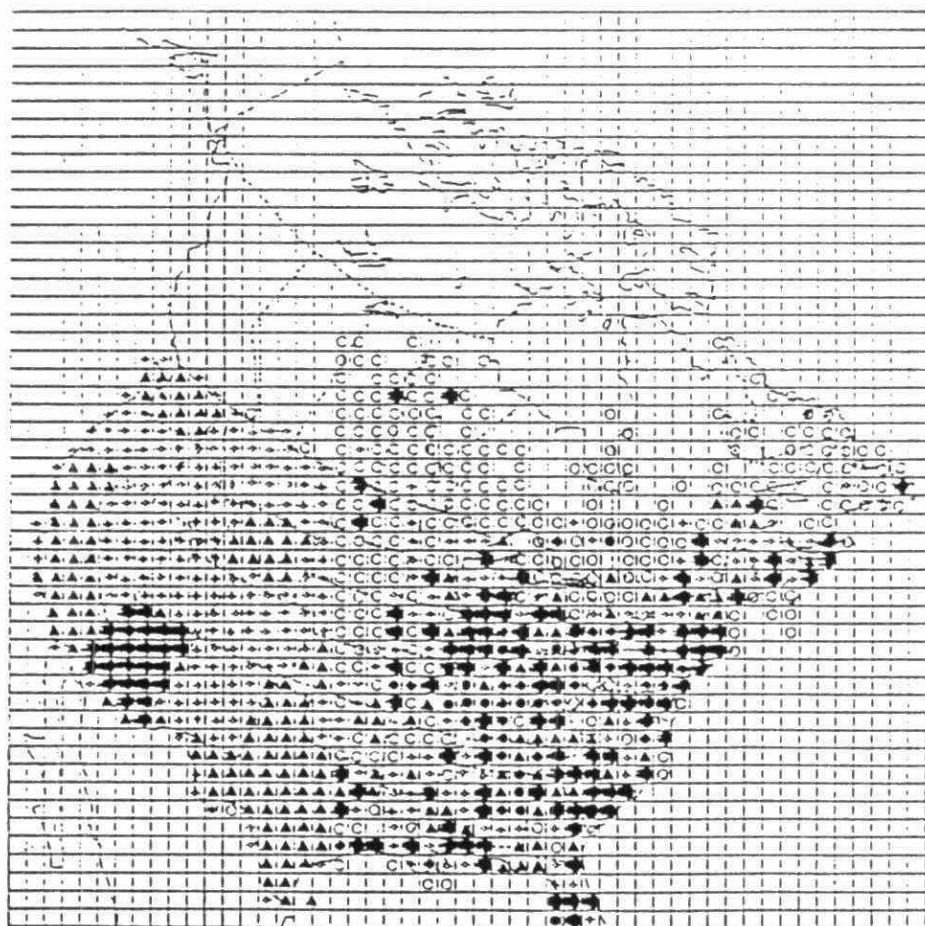


Figure 3. Dry Deposition Velocity of SO_2 .



0 500 5K 20K



100 1K 10K

Figure 4. SO₂ Emissions, g/s.

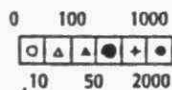
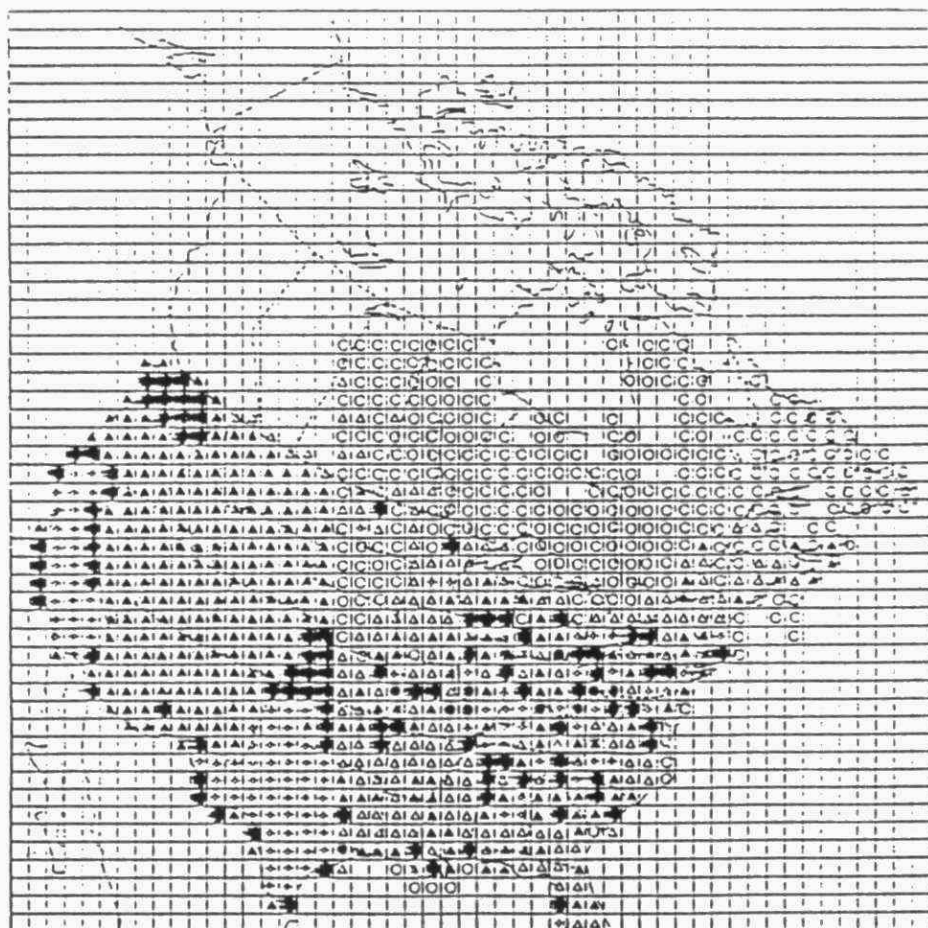


Figure 5. NO_x Emissions, g/s.

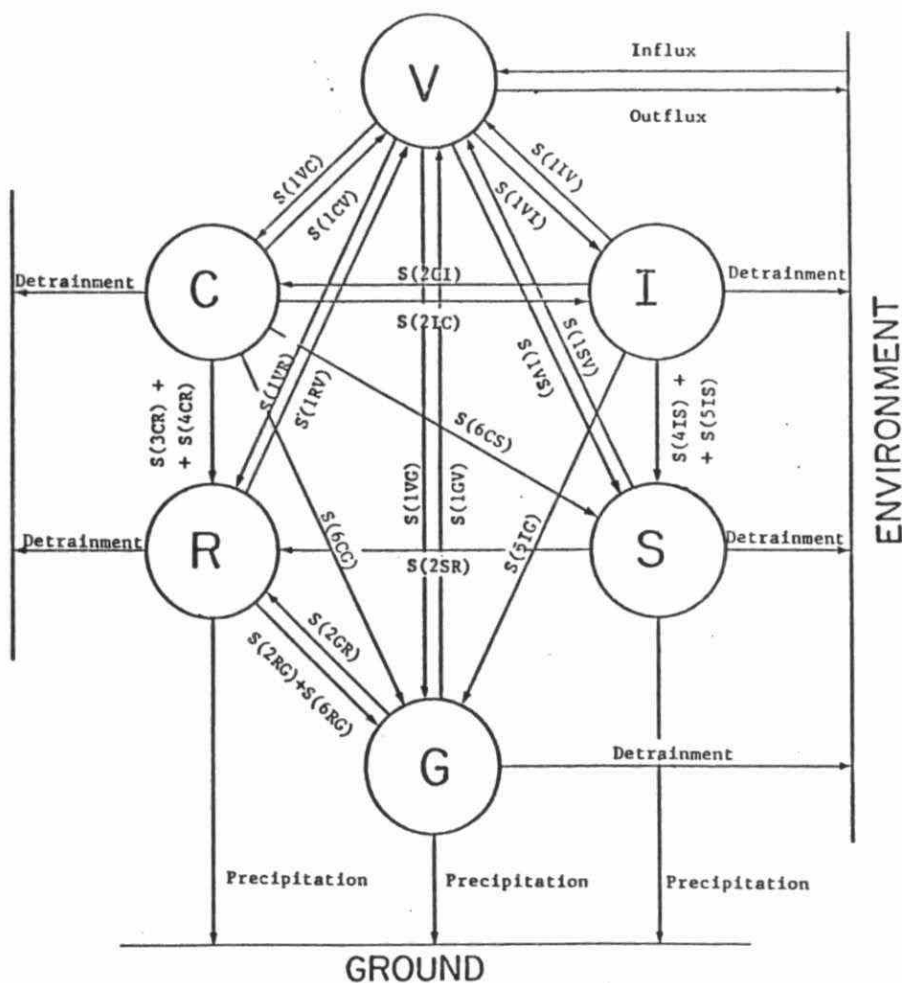


Figure 6. Microphysical interactions.

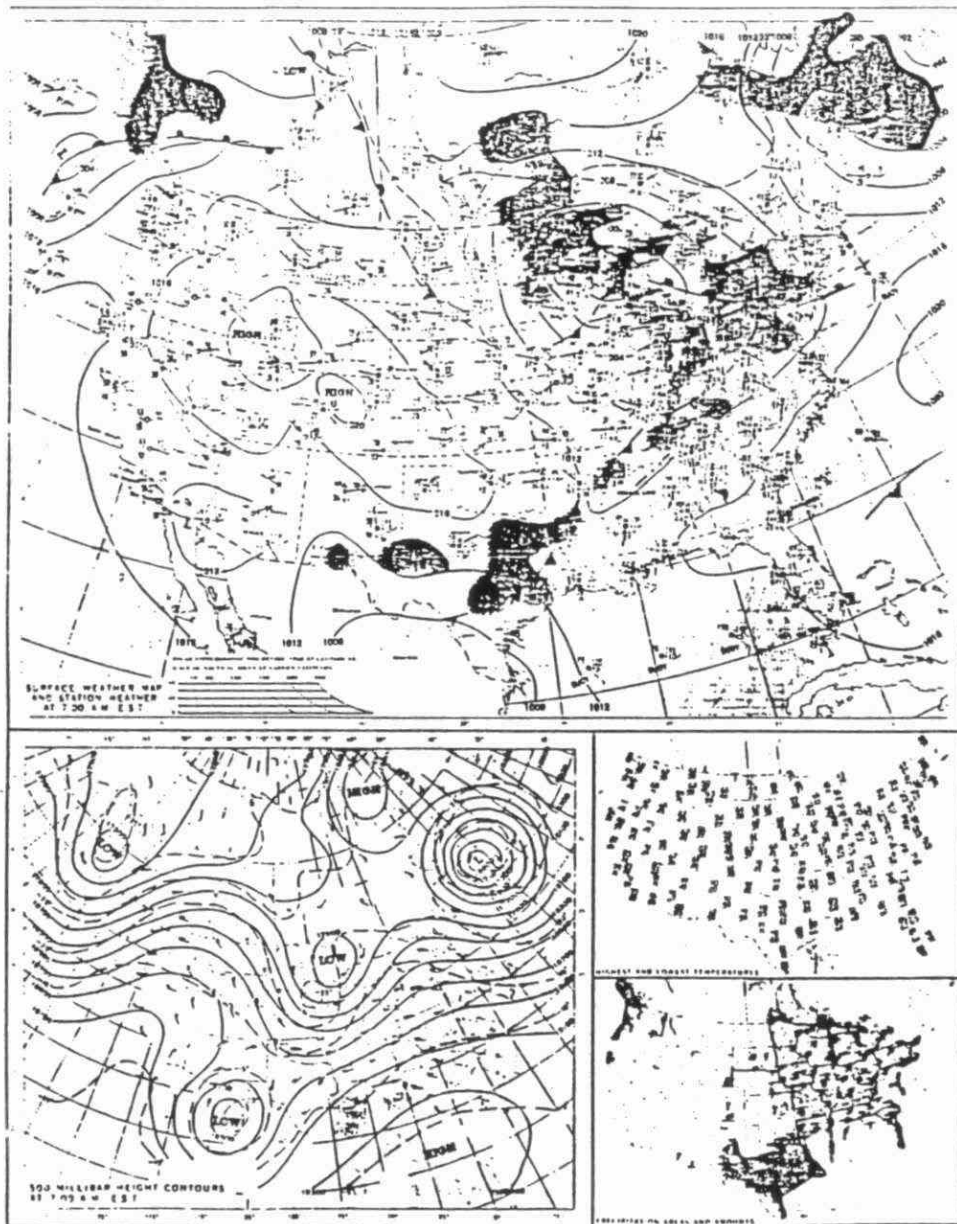


Figure 7. Surface Weather Map and the 500 mb Height Contour Map at 12 Z, April 23, 1981, the Beginning of the Simulation Period.

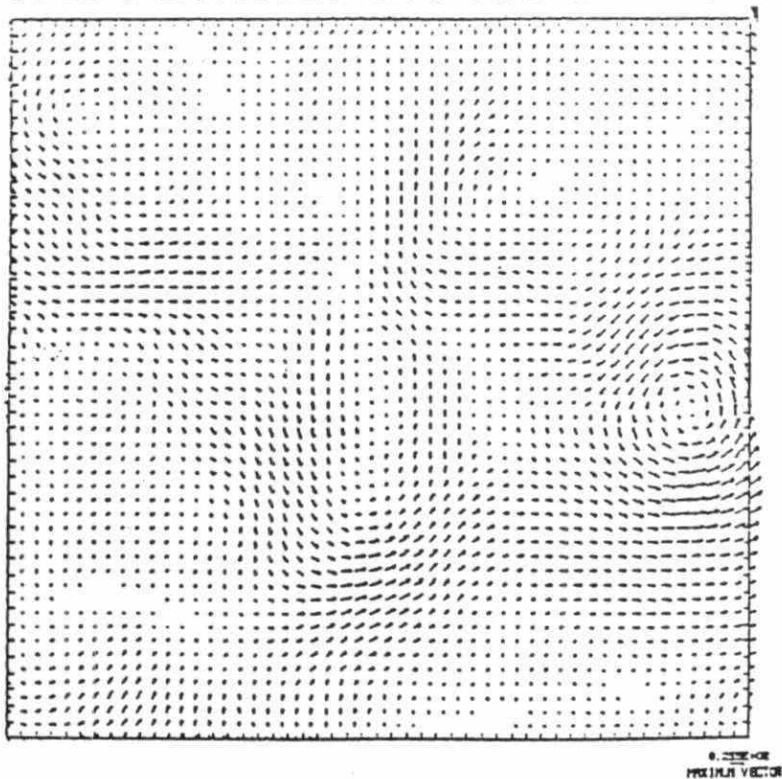
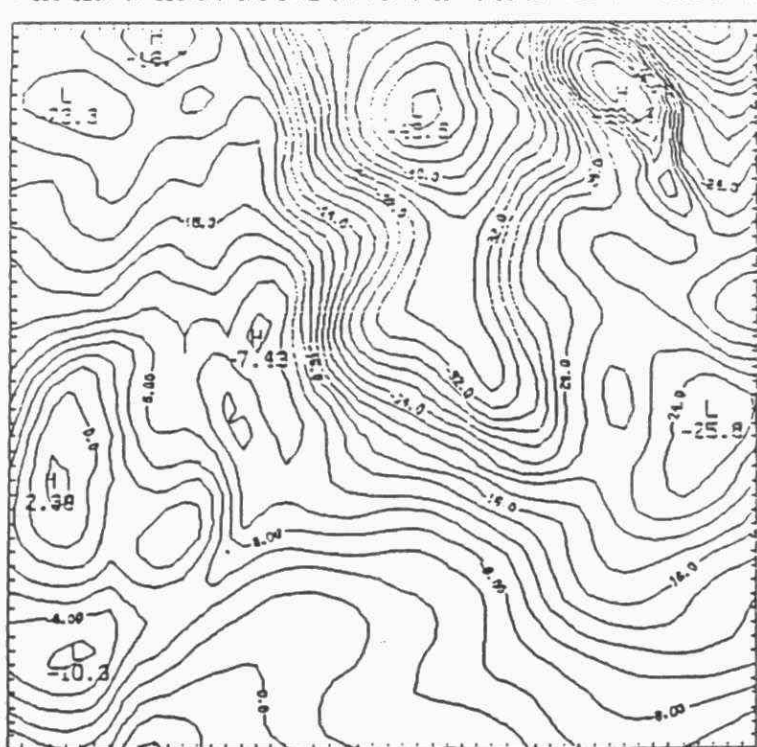


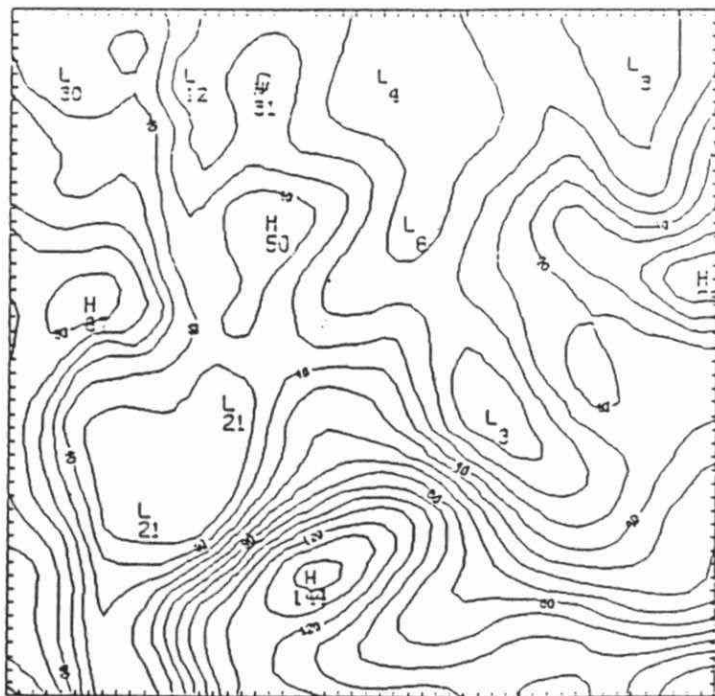
Figure 8. The Initial Wind Vector Field at the $\sigma = 0.975$ Level.

1. The first step is to identify the problem or question that needs to be addressed. This involves understanding the context and the specific requirements of the task.



CONTOUR FROM -50.000 TO 10.000 CONTOUR INTERVAL OF 2.000 PITCH = -4.231

Figure 9. The Initial Temperature Field at the $\sigma = 0.975$ Level in (T-300) K.



CONTUR FROM 0.00000E+00 TO 0.10000E+01 CONTUR INTERVAL OF 0.10000E+01 (10.0) 0.00000E+00 0.10000E+01 0.20000E+01 0.30000E+01 0.40000E+01 0.50000E+01 0.60000E+01 0.70000E+01 0.80000E+01 0.90000E+01 0.10000E+02

Figure 10. Same as in Figure 9, Except for Water Vapour Mixing Ratio in 10^{-4} kg/kg.

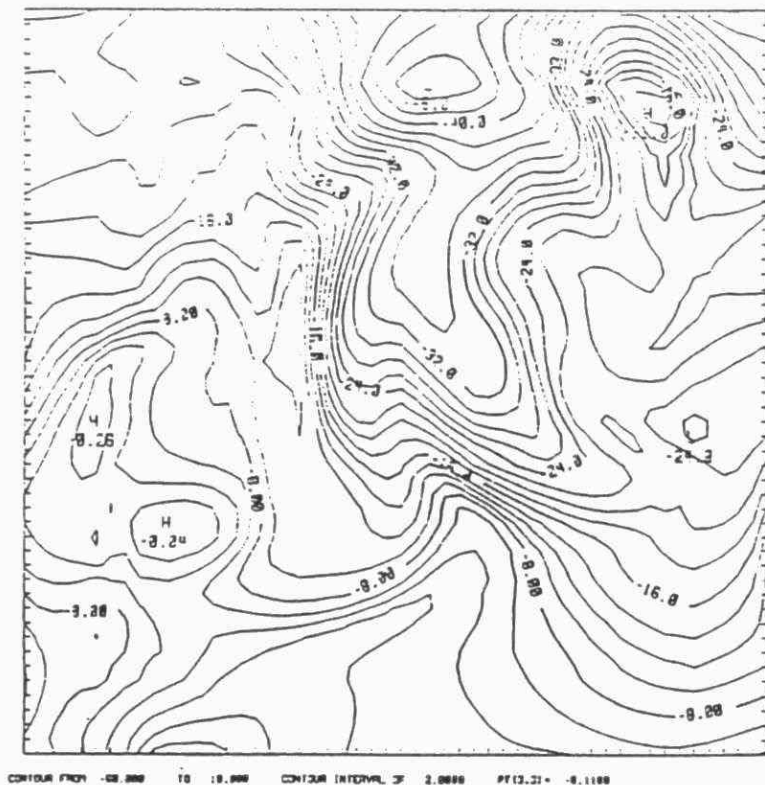
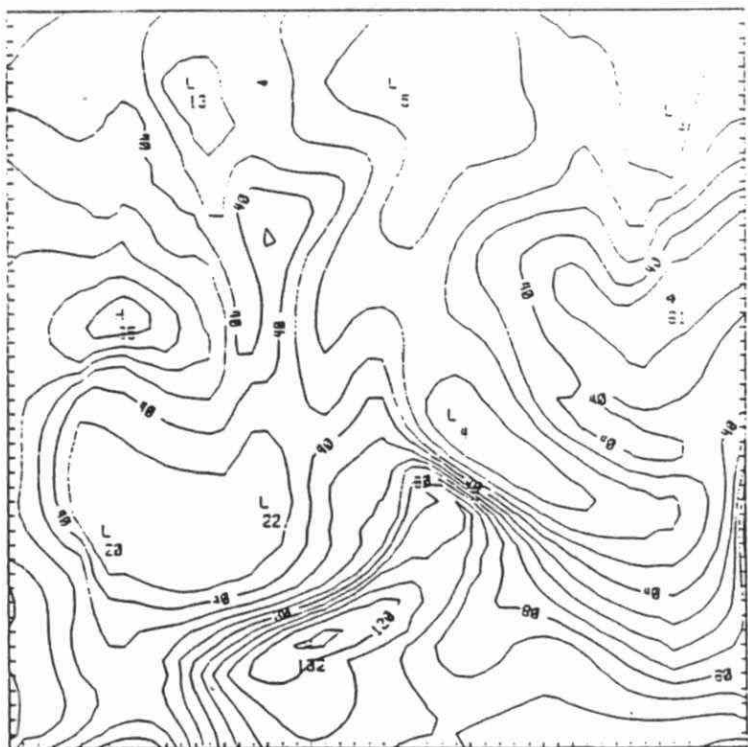


Figure 11. 12-Hour Simulated Results Showing the Temperature Field in Units of (T-300) K at the $\sigma = 0.975$ Level.



1.0000E+00 TO 8.2000E-01 CONTOUR INTERVAL OF 8.1000E-02 PT (3.3) - 8.7375E-02 LABELS SCALED BY 10000.

Figure 12. Same as in Figure 11, Except for Water Vapour Mixing, Ratio, Labelled in 10^{-4} kg/kg.

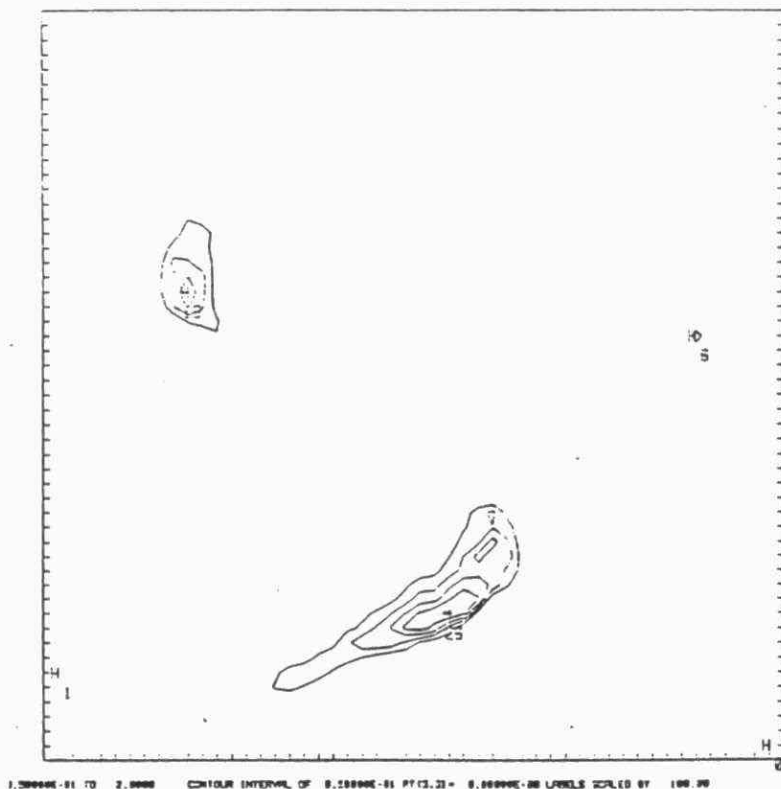


Figure 13. 12-Hour Accumulated Rainfall Labelled in 10^{-2} cm, Due to Convective Clouds Parameterized According to Kuo's Scheme.

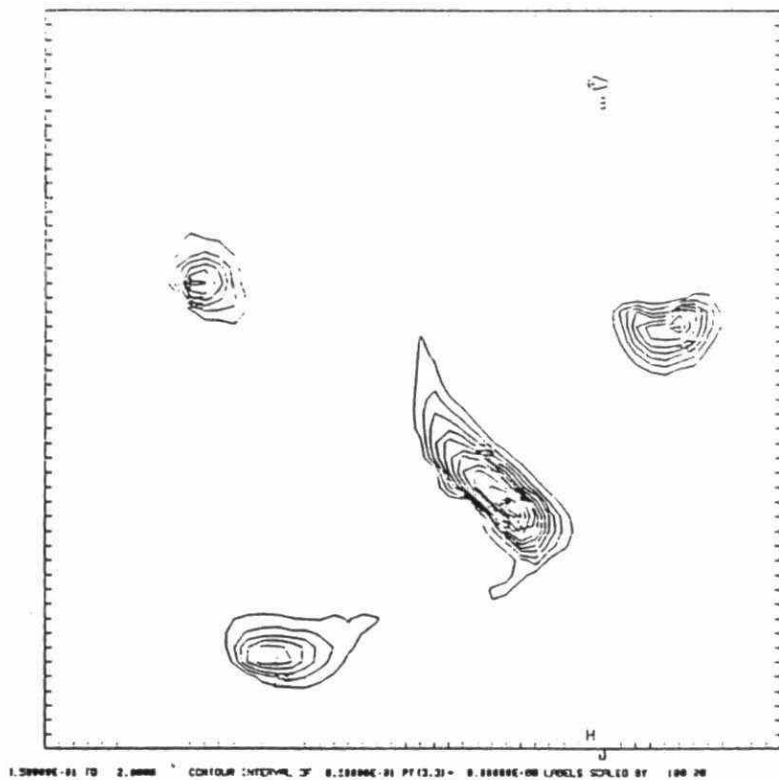
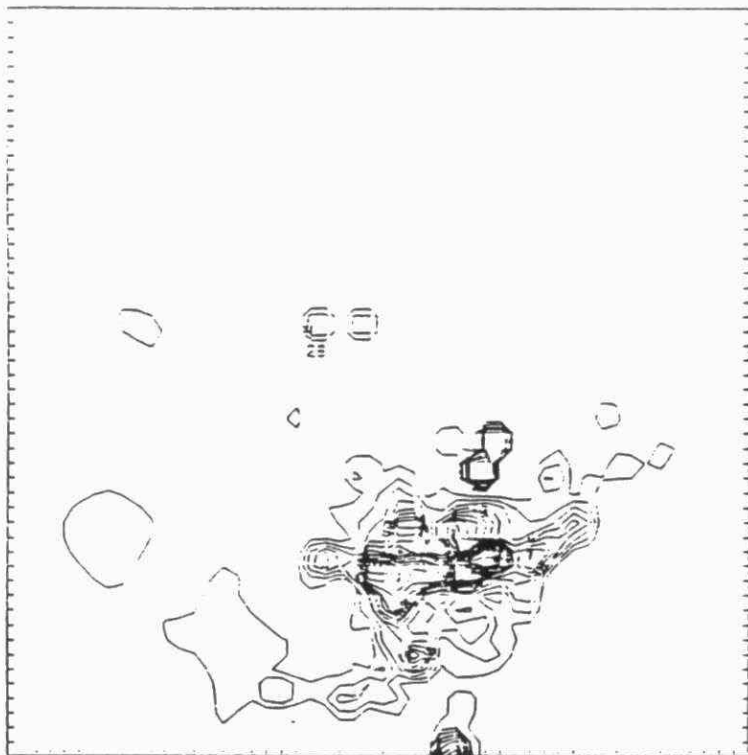


Figure 14. 12-Hour Accumulated Rainfall Due to Stratiform Clouds, Labelled in 10^{-2} cm.



0.0000E+00 TO 0.0000E+01 COLOUR INTERVAL OF 0.0000E+00 PER 0.0000E+00 LABELS SCALED BY 0.0000E+01

Figure 15. The Initial SO_2 in the Field at the $\sigma = 0.975$ Level, Labelled in 10^{-10} kg/kg.



1.0000E-08 TO 8.1000E-08 CONTOUR INTERVAL OF 0.1000E-08 PPT(2.2) = 0.0000E-08 LABELS SCALED BY 8.1000E-12

Figure 16. Same as in Figure 15, Except for NO_2 , Labelled in 10^{-11} , Volume Mixing Ratio.

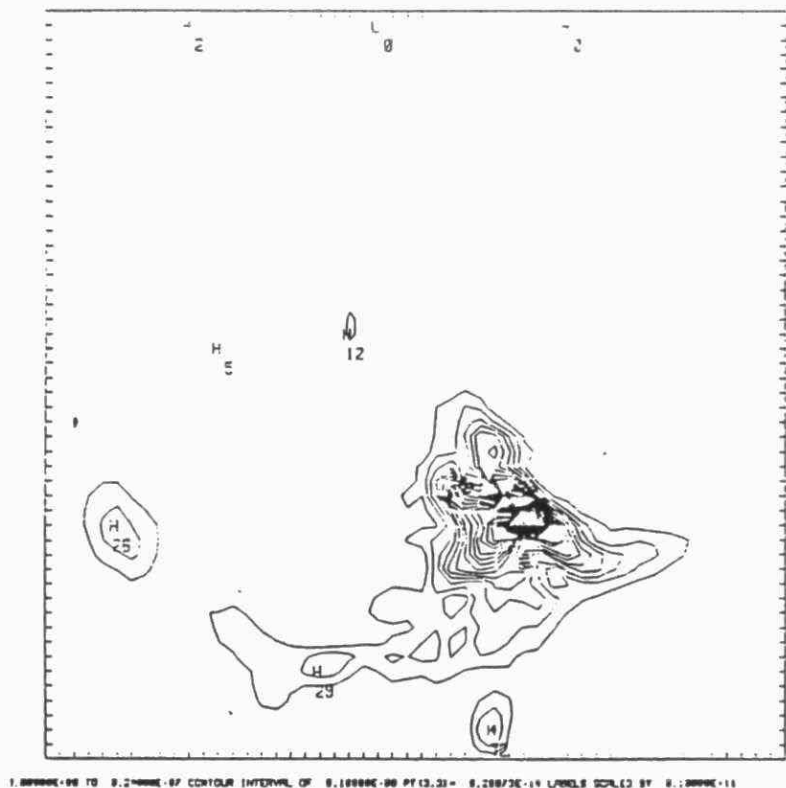


Figure 17. 12-Hour Simulation Field Showing SO_2 at the $\sigma = 0.925$ Level, Labeled in 10^{-10} , Mass Mixing Ratio.

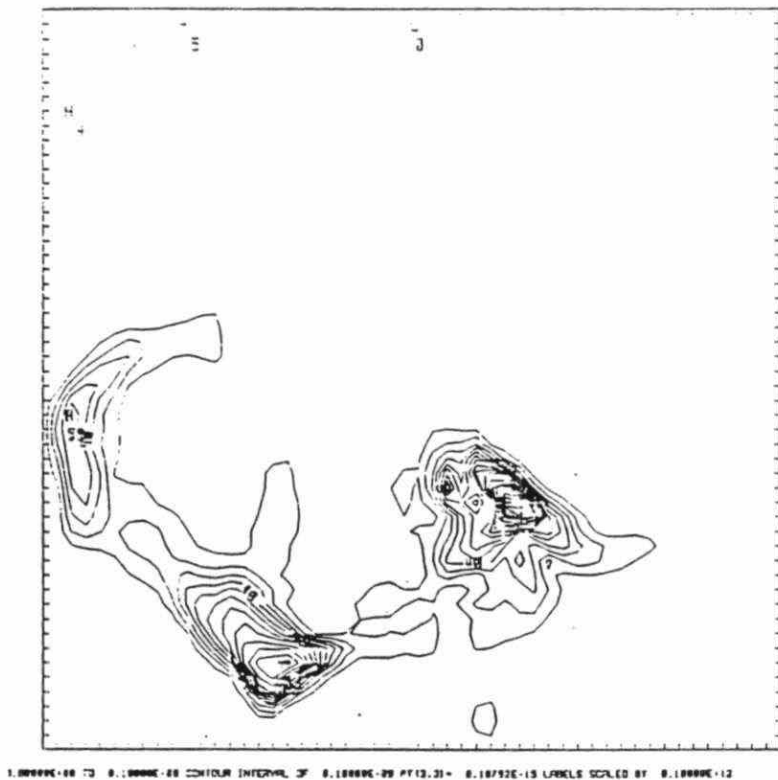


Figure 18. Same as in Figure 17, Except for NO_2 , in 10^{-11} , Volume Mixing Ratio.

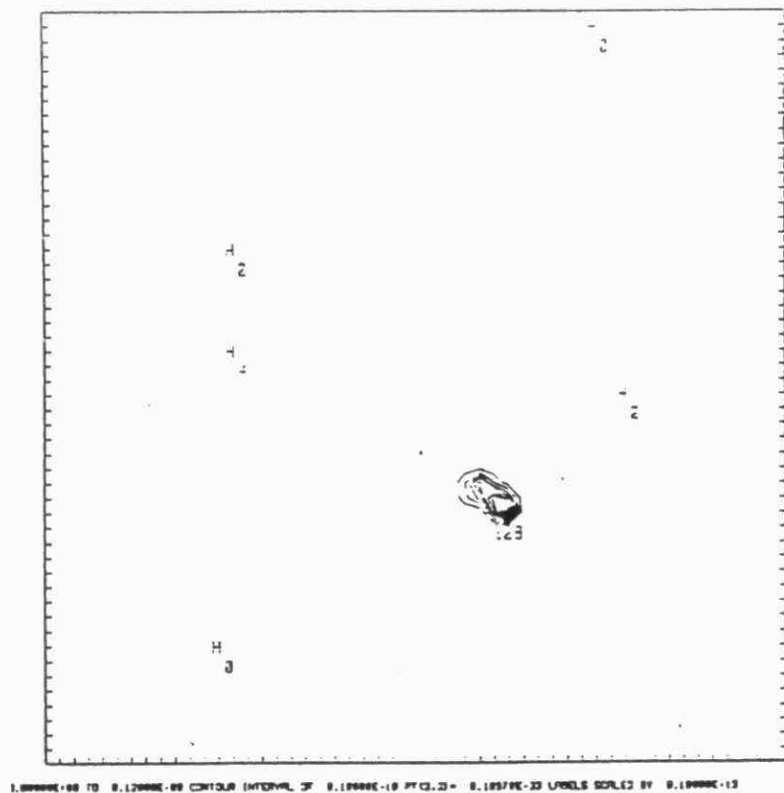
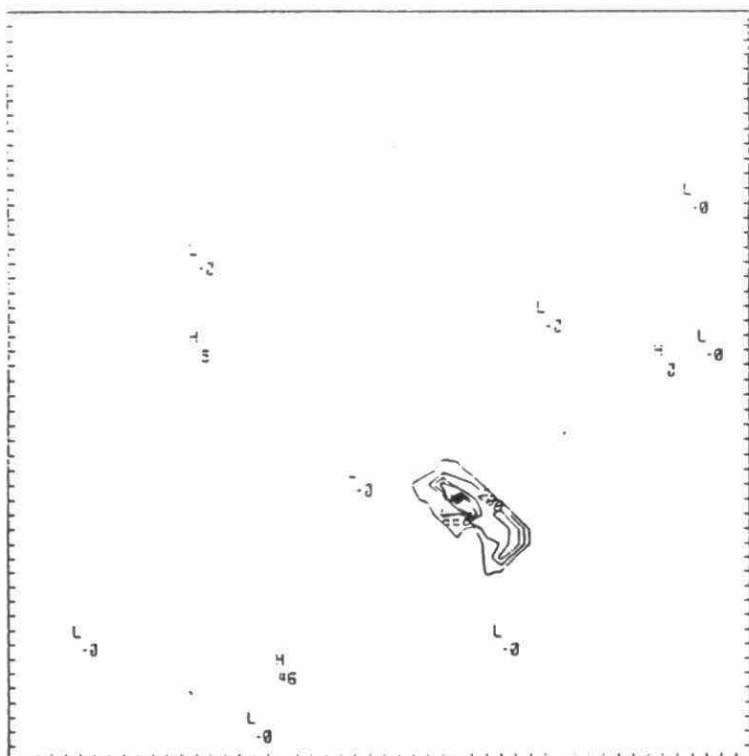


Figure 19. Same as in Figure 17, Except for SO_4 in Cloud Water, in 10^{-12} k mol/kg.



1.1000E-11 TO 0.0000E+00 CONTOUR INTERVAL OF 0.0000E-11 PFC(3,3) = 0.0000E+00 UNITS SCALED BY 0.1000E+15

Figure 21. Same as in Figure 17, Except for SO_4^{m} in Rain Water, Labelled in 10^{-14} k mol/kg of Air.



1.0000E-13 TO 0.0000E-12 CONTOUR INTERVAL OF 0.0000E-13 PT (3.21) 0.0000E-08 LPODS SCALED BY 0.1000E-16

Figure 22. Same as in Figure 17, Except for NO_3^- in Rain Water, Labelled in 10^{-15} k mol/kg of Air.

SPATIAL AND TEMPORAL VARIABILITIES
OF ACID RAIN LEVELS IN ONTARIO

by

Edward A. McBean, Michel Kompter, John Donald,
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INTRODUCTION

The monitoring of acid rain deposition levels represents an expensive, but essential task for Ontario. The specification of the intensity of the monitoring network in terms of spatial resolution is an integral part of the monitoring requirements. Uncontrollable external variable such as precipitation levels and wind direction, in addition to natural phenomena, all introduce complexities into the decisions of monitoring intensities and require that statistical interpretation of the data be utilized. It is not possible, because of the multiple source and multiple processes occurring simultaneously, to examine the intricacies of any of the ongoing processes in isolation. Instead, they must be addressed in a collective manner.

Nevertheless, the shutdown of emissions at Sudbury during a strike from the summer of 1982 to winter 1983, provided a useful opportunity to examine the changes in sulfate concentration and deposition levels as a response to removal of the largest single anthropogenic source of sulfur emissions in the world. To examine the effect of diminishing emissions, and the spatial and temporal variabilities of acid rain levels in

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Ontario in general, statistical analyses of the monitoring data were used to examine the degree of variability of concentration and deposition data (on a seasonal basis) and the possible causative roles of precipitation and wind direction. As well, the ability of monitoring locations to be used collectively in the context of an "airshed" in an attempt to obtain additional measures of deposition rate, is employed.

BACKGROUND TO SUDBURY SOURCES AND AIRSHED DELINEATION

The two mining and smelting operations near Sudbury are the source of greater than half of the total SO₂ emissions in Ontario (Tang et al, 1984). However, using deposition and air concentration data and sector stratification techniques, Chan et al (1984) concluded that only very few quantities of the sulfur compounds emitted at Sudbury are deposited close to the source (within 40 km). Most of the deposition in this area was attributed to upwind sources.

The Ontario Ministry of the Environment established the APIOS-C network in 1980, operating on a 28-day sampling period. The sampling stations were located in areas that would ensure spatial scales varying from local to regional to provincial were adequately represented. To examine acid rain phenomena, the concept of "airshed" will be utilized herein. An airshed will involve use of monitoring locations as groupings from similar areas. This procedure will prove helpful for the statistical interpretation of data. Airshed delineations employed are depicted in Figure 1.

VARIATIONS IN METEOROLOGICAL PHENOMENA

Variations in Precipitation Data

A selection of 20 gauges from those available via Atmospheric Environment Services (AES) was made to encompass southern Ontario and

Figure 1 Delineation of Airsheds and Locations
of Specific Wind Roses



the western regions of Quebec (essentially encompassing the region depicted in Figure 1). From these gauges, summary comments on the variability of the precipitation data include:

- (i) the variability of annual mean precipitation levels in a spatial sense is quite small, insofar as long-term averages are concerned, as indicated in Table 1.

Also, the precipitation levels tend to be very uniform on a seasonal basis.

- (ii) the coefficients of variation, to explore the degree of variability in a temporal sense, for each of the monitoring locations are summarized in Table 1. The uniformity of the variability in precipitation levels indicates that if the sulfate concentration levels are constant, the variability in deposition levels will be minimal, in a spatial sense, over the long-term. (Note, that this does not mean deposition levels at different locations for a single year are constant).

Variations in Wind Rose Data

A summary of statistics using the wind rose at Sudbury, as a means of quantifying seasonal variabilities in the wind directions, is presented in Table 2, for four summary quadrants. The results indicate that:

- (i) there are predominant wind directions, but these are not overwhelming. For example, the annual statistic indicates considerable uniforming, with quadrants I and III essentially identical and II and IV less in magnitude but still substantial;

Table 1 Coefficient of Variation of Precipitation Levels

Monitoring Location	Season			
	Winter	Spring	Summer	Fall
Bancroft	.33	.31	.27	.27
Biscotasing	.37	.30	.27	.26
Chalk River	.31	.32	.26	.25
Dunchurch	.27	.25	.19	.16
Kingston	.23	.23	.22	.32
London	.28	.28	.31	.27
Mt. Laurier	.31	.26	.24	.20
New Liskeard	.32	.35	.28	.41
Niagara Falls	.26	.31	.33	.36
North Bay	.23	.29	.25	.24
Ottawa	.22	.30	.29	.25
Owen Sound	.33	.30	.27	.19
Quebec	.23	.26	.26	.23
Sault St. Marie	.27	.26	.26	.22
Sudbury	.33	.32	.27	.24
Timmins	.29	.24	.21	.23
Toronto	.25	.29	.33	.28
Trois Rivières	.28	.24	.26	.24
Val d'Or	.25	.30	.21	.22
Windsor	.31	.24	.33	.34
Mean \bar{x} =	.28	.28	.27	.26
Standard S = Deviation	.042	.033	.040	.060

Notes - Means and Variances as calculated over the long term

(ii) the year-to-year variability is relatively small. A summary of the year-to-year variability is provided in the row entitled 'coefficient of variation' which indicates the standard deviation is typically 10 to 20 percent of the mean (with the exception of the 'calm' direction which has higher values but with a sufficiently small mean frequency that the importance of the calm periods is minimal).

VARIATIONS IN SULFATE CONCENTRATION DATA

Changes in Sulfate Concentrations

To examine the utility of airsheds, the annual average of SO_4 concentration levels for 1981 through 1984, were accumulated, an example of which is depicted in Figure 2. The concentration data indicate the apparent 'reasonableness' of the airshed concept (i.e. that the individual measurements within an airshed are all representative measures of the same concentration level within the airshed).

Indicated in Table 3 are the ratios of concentrations of the three shutdown periods to the long-term averages, for the north and east airsheds. The t-test indicates that for both the individual and average ratios, the mean of the ratios is significantly (at the 95 percent level) less than unity. These results indicate that the shutdowns had a significant impact on SO_4 concentration in the north and east airsheds.

ANOVA Analyses

Analysis of variance (ANOVA) is a powerful statistical technique used to isolate out the degree to which the variance of one variable is explained by the variance of another variable. The individual variables included in the analyses to follow are:

Figure 2 Mean SO_4 Concentrations for 1981 (mg/l)



1. Loichwater
2. Merlin
3. Pt. Stanley
4. Wilkesport
5. Alvinston
6. Huron Park
7. Waterloo
8. Palmerston
9. Shallow Lake
10. Milton
(removed March 1984)
11. Unbridge
12. Coldwater
13. Campbellford

14. Clovne
(replacing Kaladar
June 1983)
15. Smith's Falls
16. Delhouse Mills
17. Golden Lake
18. Wilberforce
19. Whitney
20. Dorset
21. McKellar
22. Mattawa
23. Killarney
24. Bear Island
25. Gougenda
26. Azure Lake

27. Moonbeam
28. Attawapisket
(removed February 1984)
29. Winisk
30. Geraldton
(replacing Makina
August 1983)
31. Dorion
32. Quetico Centre
33. Lac la Croix
34. Experimental Lakes Area
35. Eer Falls
36. Pickle Lake
37. Turkey Lake

Table 3 Seasonal Values of Concentrations Relative to Means, During Shut Down Periods, for the North and East Airsheds

Season	Airshed	Location	Ratio of Concentrations	
			Individual	Average
Summer 1982	North	18	.82	0.91
		19	.94	
		20	.94	
		21	1.03	
		22	.81	
	East	13	.78	0.95
		14	---	
		15	1.05	
		16	1.03	
		17	.92	
Fall 1982	North	18	1.11	1.05
		19	.93	
		20	1.06	
		21	1.17	
		22	1.00	
	East	13	.73	0.90
		14	---	
		15	.95	
		16	1.05	
		17	.87	
Winter 1983	North	18	.96	0.88
		19	.71	
		20	1.05	
		21	.90	
		22	.79	
	East	13	.79	0.80
		14	---	
		15	.59	
		16	.81	
		17	1.00	

Table 6 Single ANOVA Analyses - 50_g Concentration

Season	Total	PRECIPITATION			YEAR			STM			WIND		
		Incr.	Varia.	(%)	Incr.	Varia.	(%)	Incr.	Varia.	(%)	Incr.	Varia.	(%)
Winter	NORTH	5.56	0.73	13	2.98	54	.005	1.79	32	.183	1.84	33	.032
	EAST	7.55	0.39	5	1.83	24	.258	3.82	51	.044	1.83	24	.124
	CENTRAL	5.65	0.43	8	2.74	50	.158	1.72	32	.218	2.57	47	.078
Spring	NORTH	10.71	3.83	36	6.59	62	.001	.77	7	.879	6.59	62	.000
	EAST	12.59	0.79	6	6.62	53	.013	3.34	27	.367	6.35	50	.105
	CENTRAL	9.51	4.40	46	4.06	43	.245	1.94	20	.401	4.05	43	.108
Summer	NORTH	10.16	1.09	11	3.88	38	.048	1.21	12	.638	3.74	37	.008
	EAST	8.83	.83	9	2.67	30	.146	3.51	40	.048	2.45	28	.038
	CENTRAL	9.68	2.79	29	5.39	65	.052	1.01	11	.567	4.67	49	.034
Autumn	NORTH	3.27	1.15	35	0.90	28	.146	1.32	41	.028	0.58	18	.115
	EAST	6.75	.45	7	2.36	35	.085	1.98	29	.159	0.37	6	.567
	CENTRAL	4.53	2.69	59	1.68	37	.331	.45	10	.561	0.01	0	.986
Annual	NORTH	2.63	.93	36	1.54	59	.002	0.59	22	.400	1.48	56	.001
	EAST	3.54	.32	9	1.61	45	.033	1.54	43	.095	1.51	43	.015
	CENTRAL	1.87	.05	3	0.67	36	.344	0.64	34	.185	0.09	5	.828
Annual	NORTH	2.63	.93	36	1.54	59	.002	0.59	22	.400	1.48	56	.001
	EAST	3.54	.32	9	1.61	45	.033	1.54	43	.095	1.51	43	.015
	CENTRAL	1.87	.05	3	0.67	36	.344	0.64	34	.185	0.09	5	.828

- (i) precipitation;
- (ii) year - 1980 to 1984;
- (iii) station - the different monitoring locations within the defined airsheds (e.g. 5 monitoring locations for the northern airshed); and,
- (iv) wind direction - the percentage of time that the wind is blowing in a particular direction.

The results of the ANOVA are summarized in Table 4. For each of the seasons and each of the airsheds for a given season, a series of quantified results are provided:

- (i) Total Variability - the total variance about the mean. For example, the variance of SO_4 concentration in the north airshed in winter is 5.54 (mg/l)^2 . That is, the total variance using the 5 monitoring locations in the airshed for all of the available data (1980-84).
- (ii) Inc. Variability - for the parameter indicated (i.e. precipitation, year, station, and wind direction), this is the incremental variability of SO_4 concentration explained by the variability of parameter. For example, precipitation explains 0.73 (mg/l)^2 of the concentration data variance.
- (iii) Inc. Variability (%) - this is the percentage that (ii) represents of (i).
- (iv) $PR > F$ - This is the actual statement of the probability of the hypothesis being true. If this column contains a value less than .05 then the null hypothesis is rejected, i.e. the independent variable (e.g precipitation) significantly explains the variability of SO_4 concentration at a 95 percent level of significance.

The ANOVA findings indicate:

- (i) precipitation does not significantly explain (at the 95% level) the variability in the SO_4 concentrations, within an airshed. i.e. precipitation doesn't have an important 'lowering' or scavenging effect on SO_4 concentration levels;
- (ii) year-to-year (time was input simply as a linear trend) is occasionally a good explanatory variable of SO_4 concentrations. Since emission levels are not expected to have changed linearly over the 1980 to 1984 time period, this associative behavior is expected to have been identified simply as a correlative behavior with other variables;
- (iii) station variability does not significantly explain the SO_4 concentration variability within an airshed. This finding supports the concept of airshed since it means that individual measures from the stations are not explaining much of the variability in the concentrations; and,
- (iv) wind directions indicated a considerable importance in particular for the northern airshed and a lesser importance to the eastern airshed. For the central and western airsheds, the wind direction was not statistically significant but it must be noted that the wind doesn't blow very frequently from Sudbury to the central and western airsheds and thus, this finding is not very surprising.

A summary tabulation of the statistically-significant (at the 95 percent level) sources of variance for SO_4 concentration levels is provided in Table 5.

Table 5 Summary of Averages of Percent of Variances Explained From Single ANOVA Analysis for SO₄ Concentration

	Precipitation	Year	Station	Wind
North	26	48	23	41
East	7	37	38	30
Central	29	46	21	29
West	31	32	37	14

Since the earlier determination indicated that emissions from Sudbury had a significant impact on concentrations, ANOVA tests were examined with the periods of shutdown removed from the data set, (i.e. removal of summer 1982, fall 1982 and winter 1983). The results from the single variable ANOVA are contained in Table 6; a comparison with Table 4 indicates rather small changes. The summary of averages of percent of variances explained (without the period of Sudbury shutdown included) for SO₄ concentration are indicated in Table 7.

Table 7 Summary of Averages of Percent of Variances Explained From the Single ANOVA Analyses for SO₄ Concentration, Without Sudbury Shutdown Data

	Precipitation	Year	Station	Wind
North	25.4	50.2	20.4	41.0
East	19.6	30.2	46.8	22.2
Central	38.4	55.4	20.2	53.6
West	33.6	27.2	38.6	20.4

The summation effect of multiple variables on the ANOVA are indicated in Table 8. Several points are noteworthy, namely:

- (1) the combination of variables assist in explaining the variability of concentration data particularly for the northern and eastern airsheds; and,

Table 6 Single ANOVA Analyses - SO_2 Concentration (Without Substudy Shutdown Data)

Season	Total	Precipitation				Year				Site				Wind			
		Incr.	Varia.	(%)	Pr>F	Incr.	Varia.	(%)	Pr>F	Incr.	Varia.	(%)	Pr>F	Incr.	Varia.	(%)	Pr>F
Winter	4.33	1.23	.282		2.67	.62	.003		1.52	.63	.506		1.54	.36	.019		
	5.57	.28	.755		.29	5	.741		1.31	23	.043		.29	5	.431		
	6.00	1.91	.806		2.70	59	.111		2.08	23	.513		2.53	55	.036		
	WEST	6.00	1.78	.259		2.16	36	.069		2.23	37	.280		1.09	18	.113	
Spring	10.71	3.83	.065		6.59	62	.001		.77	7	.879		6.59	62	.000		
	12.59	0.79	.612		6.62	53	.013		1.94	27	.267		4.05	50	.108		
	9.51	4.40	.202		4.06	43	.245		3.34	20	.401		6.35	43	.005		
	CENTRAL	9.51	4.40	.202		4.06	43	.245		3.34	27	.401		6.35	50	.108	
Summer	8.58	.44	.654		2.66	31	.125		.99	12	.768		2.52	29	.062		
	7.17	2.96	.113		1.76	25	.253		4.36	61	.011		1.55	22	.160		
	8.35	2.82	.659		6.11	73	.038		.43	35	.833		5.78	3	.016		
	WEST	3.88	.210		.59	5	.853		4.17	35	.170		.36	3	.780		
Autumn	2.76	.76	.151		.91	33	.087		.89	32	.184		.41	15	.093		
	6.07	1.41	.180		2.08	34	.107		2.05	5	.220		.03	0	.778		
	3.22	1.91	.185		.97	30	.446		.15	5	.829		.94	2	.251		
	WEST	2.79	.037		4.13	60	.002		1.24	18	.533		3.31	48	.004		
Annual	1.88	.57	.280		1.19	63	.006		.47	25	.792		1.19	63	.006		
	1.16	.26	.710		.40	.099	.099		.57	49	.511		.40	34	.099		
	.60	.20	.312		.43	.069	.069		.01	2	.986		.43	72	.069		
	WEST	1.53	.556		.27	18	.230		1.02	67	.171		.27	17	.230		
Average																	
29.3				40.8				30.5				11.8					

Table 8 Multiple ANOVA Analysis SO_4 Concentration

Model of SO ₄ Tr. = Precip. and Wind				Model of SO ₄ Tr. = Precip. Stn. and Wind						
Season	Total Varia.	Incr. Varia. (%)	Pr>F	Season	Total Varia.	Incr. Varia. (%)	Pr>F	Change in Varia. with station (%)		
Winter	NORTH	5.54	2.47	45	Winter	NORTH	3.93	71	.068	
	EAST	7.56	2.21	29	EAST	7.56	5.26	70	.091	
	CENTRAL	5.46	4.74	87	CENTRAL	5.46	4.94	90	.331	
Spring	WEST	8.38	3.53	42	WEST	8.38	6.25	75	.080	
	NORTH	10.71	7.68	72	Spring	NORTH	10.71	9.32	87	.002
	EAST	12.40	7.40	59	EAST	12.40	10.53	84	.009	
Summer	CENTRAL	9.52	7.11	75	CENTRAL	9.52	8.95	94	.072	
	WEST	9.64	3.08	32	WEST	9.64	6.79	70	.133	
	NORTH	10.17	3.83	38	Summer	NORTH	10.17	5.11	50	.217
Fall	EAST	8.83	4.08	46	EAST	8.83	6.28	71	.040	
	CENTRAL	9.49	6.14	65	CENTRAL	9.49	7.15	75	.360	
	WEST	34.95	16.39	47	WEST	34.95	18.36	52	.266	
Annual	NORTH	3.27	3.47	45	Fall	NORTH	3.27	1.89	58	.078
	EAST	6.75	1.07	16	EAST	6.75	4.02	60	.106	
	CENTRAL	4.54	2.78	61	CENTRAL	4.54	3.26	72	.315	
Annual	WEST	9.06	6.47	71	WEST	9.06	7.44	82	.001	
	NORTH	2.62	1.74	66	Annual	NORTH	2.62	2.22	85	.011
	EAST	3.54	1.98	56	EAST	3.54	2.99	84	.045	
Annual	CENTRAL	1.87	0.22	12	CENTRAL	1.87	1.25	67	.607	
	WEST	4.15	0.64	15	WEST	4.15	3.41	82	.022	

- (ii) all three components contribute substantially to the explanation of variability in concentration data.

VARIATIONS IN DEPOSITION LEVELS

In analyses similar to those undertaken as the concentration data, statistical analyses were carried out on the deposition rate information. The findings, some of which are indicated in Table 9, include:

- (i) there is large variability from one location to another, and, from year-to-year the magnitudes of deposition at a single location fluctuate considerably; also,
- (ii) there are substantial differences in deposition rates for different seasons; and,
- (iii) there are no apparent trends over time in deposition rate, including any apparent widespread reduction during the periods of shutdown in Sudbury.

ANOVA Analyses on SO₄ Deposition Rates

The results of the ANOVA tests are summarized in Table 10. The findings include:

- (i) 'year' shows a surprising degree of statistical significance. Since emissions in general are not expected to have changed linearly with time, the statistical significance is expected to be the result of correlative behavior with other variables;
- (ii) 'station' - with the exception of the northern airshed for two seasons (winter and fall), 'station' is not statistically significant. These results indicate the apparent reasonableness of treating the individual monitoring stations as all representative of the deposition rate within the airshed.

Table 9 SO₄ Depositions (kg SO₄/ha) for a Series of
Individual Seasons and Monitoring Locations

Station Name	Location	Year	Winter	Spring	Summer	Fall	Annual
Alvinston (1081)	5	80	----	----	14.99	6.45	----
		81	7.41	9.74	19.69	7.68	44.52
		82	6.89	10.46	9.57	6.67	33.60
		83	4.93	13.85	12.46	4.93	36.17
		84	7.00	11.89	14.84	6.19	39.91
Huron Park (1191)	6	80	----	----	----	----	----
		81	----	----	----	9.86	----
		82	8.08	15.10	12.56	7.47	43.21
		83	4.71	9.79	14.10	3.61	32.21
		84	6.83	16.43	7.99	6.72	37.96
Waterloo (2021)	7	80	----	----	7.58	6.38	----
		81	5.20	11.05	16.11	7.45	39.81
		82	6.08	11.54	12.42	3.42	33.46
		83	5.48	13.47	9.81	4.48	33.24
		84	4.92	9.99	11.58	6.26	32.74
Palmerston (1101)	8	80	----	----	11.62	10.29	----
		81	4.77	11.98	18.67	7.39	42.82
		82	8.41	9.65	8.92	8.86	35.83
		83	3.76	8.58	8.84	4.01	25.19
		84	6.97	8.51	10.39	6.90	32.77
Cambellford (3081)	13	80	----	----	5.51	6.55	----
		81	4.54	10.38	15.54	3.86	34.32
		82	4.46	13.36	8.35	3.50	29.68
		83	3.89	9.83	8.78	5.13	27.63
		84	3.61	6.91	12.73	6.07	29.32
Smith's Falls (4061)	15	80	----	----	12.30	6.78	----
		81	3.45	12.61	16.62	4.88	37.56
		82	2.97	7.43	8.98	3.69	23.06
		83	2.41	5.64	9.53	4.34	21.92
		84	3.06	8.79	8.99	4.00	24.85
Dalhousie Mills (4071)	16	80	----	----	13.42	8.26	----
		81	5.63	9.11	13.82	4.57	33.13
		82	2.95	12.11	9.87	4.33	29.26
		83	4.93	10.34	8.27	4.51	28.05
		84	3.17	7.28	11.26	5.88	27.59
Golden Lake (4081)	17	80	----	----	11.31	3.77	----
		81	3.98	13.44	12.04	4.10	33.57
		82	0.69	8.80	4.60	2.40	16.49
		83	2.40	7.13	8.59	2.52	20.64
		84	2.53	6.14	8.37	3.01	20.04

Table 10 Single ANOVA Analyses - SO₄ Deposition

		YEAR				STN			WIND		
Season		Total Varia. (x10 ⁶)	Incr. Varia. 10 ⁶	Incr. Varia. (%)	Pr>F	Incr. Varia. 10 ⁶	Incr. Varia. (%)	Pr>F	Incr. Varia. 10 ⁶	Incr. Varia. (%)	Pr>F
Winter	NORTH	29.0	7.0	24	.202	15.9	55	.013	4.6	16	.232
	EAST	39.7	14.4	36	.089	19.0	48	.060	14.3	36	.035
	CENTRAL	21.9	14.5	66	.044	2.1	10	.659	12.6	58	.032
	WEST	27.5	10.5	38	.048	7.0	26	.319	10.5	38	.017
Spring	NORTH	125.6	55.5	44	.022	31.8	25	.324	44.0	35	.026
	EAST	121.0	56.9	47	.027	26.5	22	.485	55.0	45	.011
	CENTRAL	67.5	3.4	5	.942	28.7	42	.110	3.0	5	.831
	WEST	184.9	44.9	24	.205	42.0	23	.391	1.4	1	.934
Summer	NORTH	864.1	300.6	35	.074	166.2	19	.372	283.9	33	.015
	EAST	270.4	159.7	59	.002	42.5	16	.517	116.8	43	.004
	CENTRAL	126.4	84.5	67	.045	.09	0	.996	79.8	63	.007
	WEST	244.3	90.9	37	.055	14.0	6	.880	75.5	31	.021
Autumn	NORTH	76.6	22.2	29	.127	42.0	55	.002	8.7	11	.263
	EAST	42.1	15.3	36	.073	15.4	37	.070	13.1	31	.023
	CENTRAL	61.9	33.7	55	.100	9.3	15	.407	19.9	32	.117
	WEST	57.7	27.3	47	.009	6.0	10	.678	19.5	34	.011
Annual	NORTH	685.1	323.0	47	.015	264.6	39	.100	307.5	45	.006
	EAST	683.2	412.7	60	.004	249.4	37	.176	412.7	60	.001
	CENTRAL	278.9	166.3	60	.081	24.8	9	.689	18.4	7	.760
	WEST	557.8	262.5	47	.015	15.6	3	.978	113.0	20	.146

Table 11 Multiple ANOVA Analysis - SO_4 DepositionModel of SO_4 Dep. = Stn. and Wind Direction

Season		Total Varia. ($\times 10^6$)	Incr. Varia. ($\times 10^6$)	Incr. Varia. (%)	Pr>F
Winter	NORTH	29.0	20.5	71	.006
	EAST	39.7	30.5	77	.005
	CENTRAL	21.9	14.6	67	.109
	WEST	27.5	17.5	64	.020
Spring	NORTH	125.6	75.8	60	.034
	EAST	121.0	66.3	55	.119
	CENTRAL	67.5	34.0	50	.307
	WEST	184.9	43.5	24	.678
Summer	NORTH	864.1	442.7	51	.036
	EAST	270.4	144.3	53	.035
	CENTRAL	126.8	84.4	67	.046
	WEST	244.3	90.7	37	.188
Fall	NORTH	76.6	47.4	62	.004
	EAST	42.1	22.5	54	.033
	CENTRAL	61.9	29.7	48	.167
	WEST	57.7	25.5	44	.072
Annual	NORTH	685.1	572.2	84	.000
	EAST	683.2	599.7	88	.000
	CENTRAL	278.9	40.6	15	.896
	WEST	557.8	128.6	23	.690

- (iii) frequency of wind direction is statistically significant in a number of seasons and airsheds.

Results of multiple ANOVA tests are included as Table 11.

CONCLUSIONS

The findings from the statistical analyses of sulfate concentration and deposition data include:

- (i) The variability in precipitation in a spatial sense over Southern Ontario, is quite small over the long-term. If the sulfate concentration levels are constant, the variability in annual deposition levels will be small in a spatial sense, over the long term. Note that this does not mean that deposition levels within a single year are constant.
- (ii) Precipitation does not have an important "scavenging effect" that reduces the sulfate concentration levels, within an airshed.
- (iii) There are predominant wind directions but the frequency in any small set of directions, is not overwhelming. The temporal variability (from year-to-year) in the wind rose is relatively small.
- (iv) Monitoring data support the 'reasonableness' of an airshed concept, namely that the individual measurements within an airshed are all measures of the same concentration and deposition levels within the airshed.

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MODELLING THE PHOTOCHEMICAL DECOMPOSITION OF CHLORINATED PHENOLS BY SUNLIGHT

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The objective of this work is to estimate the importance of the direct solar photodegradation of chlorinated phenols as a sink for these compounds in the atmosphere. Generally, the decomposition of any atmospheric pollutant by sunlight depends upon four factors: the solar radiation flux, the pollutant concentration, the pollutant absorption spectrum, and the quantum yield (or efficiency) of the photochemical decomposition. The former two quantities are available from the literature, the latter two by experimental measurement. Table 1 is a summary of the quantum yields obtained in our laboratory.

Table 1. Quantum Yields of Decomposition of Chlorophenols

Substituents	Quantum Yields, ϕ	Decomposition Rate % per hour
2-Cl	0.45 \pm 0.07	0.024
3-Cl	0.18 \pm 0.05	3.5
4-Cl	0.12 \pm 0.03	0.022
2,4-Cl ₂	0.064 \pm 0.02	0.11
3,4-Cl ₂	0.16 \pm 0.05	6.5
2,4,5-Cl ₃	0.097 \pm 0.02	2.3
Cl ₅	0.018 \pm 0.007	6.2

By combining the data on quantum yields with the absorption spectrum of the compound and literature data on solar flux, we have been able to estimate the decomposition rate in percent per hour (see Table 1) by the use of the equation below.

$$\text{Decomposition rate} = 230.3 \phi \sum \epsilon'_\lambda I_o(\lambda)$$

In this equation the summation term accounts for the absorptivity of the pollutant (ϵ') per dm of height, and I_o is the solar flux per unit area. Both of these quantities are strongly wavelength dependent. These

decomposition rates refer to full sunlight in summer at 40°N latitude. There is a general trend towards lower quantum efficiency as the number of chlorine atoms in the phenol increases, but this effect is more than offset by increased spectral overlap. Thus 2-chlorophenol, although it is intrinsically the most photolabile of all the compounds studied, according to the measure of quantum yield, is predicted to degrade the most slowly in sunlight (half life ~ 1 year). Conversely pentachlorophenol has the lowest quantum yield for decomposition, yet is predicted to be the most reactive in the atmosphere (half life < 1 day).

The direct photolysis rates have also been compared with the rates of attack on the same substances by hydroxyl (OH) radicals, another important reaction pathway for volatile organic compounds. The chlorophenol family has members both more reactive by solar photodecomposition (e.g. pentachlorophenol) and members such as 2-chlorophenol which are predicted to react principally with OH radicals, because their photochemical reactions are so slow.

Scoring System for the Prioritization of Environmental Contaminants

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There are thousands of chemical substances which have the potential to be released into various environmental media, e.g. water, air, soil and sediment. It is not possible to evaluate simultaneously the impact of all of these chemicals on biota and on the abiotic environment. In order to employ effectively the limited resources available, a number of regulatory agencies identify chemicals of concern by developing scoring systems as tools for assigning priority rankings.

Scoring systems have been designed and utilized in various ways according to the needs of the user, for example, for identifying potentially hazardous food additives or for ranking substances according to their potential to bioaccumulate. The approach used may be qualitative, resulting in a relative ranking of chemical groups into low, moderate or high levels of concern, or quantitative, resulting in a group of scores or a single aggregate score reflecting the relative hazard associated with a given chemical. A common quantitative approach is to assign numerical scores according to a substance's physicochemical and toxicological properties, thus providing a common basis for comparing different substances.

The scoring system described in this paper was developed for the Ontario Ministry of the Environment's Hazardous Contaminants Coordination Branch (HCCB), and is the product of several years' effort by the Ministry's Priority List Working Group in cooperation with the consulting firms CanTox Inc. and SENES Consultants Ltd. It is a quantitative system based on the use of vectors to describe the key properties or characteristics of chemicals. A vector consists of a set of elements, each corresponding to a property or effect relevant to the assessment of the potential environmental or health effects of a given chemical. These elements take into consideration the behaviour of a chemical in the environment, potential for exposure, and adverse effects on biota, including humans. The magnitude of the score assigned to an element reflects the level of concern arising from the property or effect that element represents. The various scoring elements employed in the system and the scoring scheme currently in use by the HCCB appear in Appendix A.

In addition to the numerical value assigned to an element, several non-numeric symbols are used as score modifiers, indicating certain concerns regarding the source of or confidence in the available data. If data are lacking, an asterisk (*) is assigned to an element in lieu of a numerical score. If data used for scoring purposes are questionable (e.g. the data were derived from studies on sites which may not represent the conditions in Ontario, documentation was incomplete, or outdated methodologies were employed), a score is assigned but is modified with a question mark (?). If the data used are perceived as representing a worst-case situation (e.g. data from studying an accidental spill or toxicity data generated from an experiment using intravenous administration), the element score is modified with an exclamation mark (!). If the data used in assigning a score to an element were derived from environmental modelling techniques, or from structure-activity relationships, the score for that element is modified with a symbol indicating estimation (e).

This evaluation scheme results in the generation of a series of scores reflecting the information characterizing the potential hazard to the environment and biota associated with a particular chemical substance. The assignment of separate scores to a set of exposure and toxicity elements provides a more comprehensive and meaningful representation of information than can be shown if only a single numerical value was assigned. Using this methodology, information is retained and areas identified for which additional research initiatives should be considered.

The individual parameter scores are combined in specific ways to provide a priority ranking for the chemicals being assessed. A specific approach to element score combination was developed to meet the HCCB's objectives (Appendix B); however, the needs of other users can be addressed by modification of the combining rules. The combining rules employed in the HCCB's version of the system have been designed to assign chemicals to high, intermediate or low priority lists based on either relatively high scores in specific elements or on combinations of scores in groups of selected elements.

The overall scoring process employed by the HCCB, for the purpose of identifying chemicals of top priority for detailed study and ultimately for standards development, is divided into three phases. Each phase requires more specific information about the subject chemical than the preceding phase. Chemicals are ranked using the elements and scoring criteria for a given phase, and if the resulting concern rating is sufficiently high they are scored again using the elements and criteria for the next phase. Table 1 lists the parameters used in the various evaluation phases.

Phase 1 defines the input into the scoring system, i.e. data on chemicals of potential concern derived from the open literature, lists of substances released by recognized agencies having regulatory and assessment responsibilities, and results of monitoring surveys relevant in reference to Ontario's environment.

Phase 2 represents a preliminary assessment employing six exposure elements, two toxicity elements and one element assessing undesirable aesthetic effects. The environmental transport element examines the percentage mass partitioning of a chemical amongst various media and examines environmental concentration data for air, water, soil, sediment, plants and animals. Release data from known sources is used, or alternatively mass distribution is estimated using the environmental transport (fugacity) model developed by Mackay and Paterson (1982). The Phase 2 element criteria are based largely on physicochemical properties and adverse effects data readily available from secondary data sources such as review articles and standard reference texts. Chemicals assigned a high priority in Phase 2 are assessed in Phase 3 first, followed by those assigned intermediate priority. Chemicals which cause undesirable aesthetic effects are automatically passed on to Phase 3 assessment.

Phase 3 of the system contains six exposure elements (taking into account environmental concentrations in multiple media) and seven toxicity elements. The score for undesirable aesthetic effects is carried over from the Phase 2 evaluation. More effort and resources are needed for Phase 3 than for Phase 2. Primary reference sources from a number of databases represent the main information sources. Once scores are generated the chemical is assigned to one of five lists: high priority, intermediate priority, low priority, inadequate information and undesirable aesthetic effects. Chemicals which are assigned to the high priority list receive first consideration for standards development.

To date, 32 chemicals have been fully assessed as part of the development and testing of the scoring system and an additional 200 chemicals have been evaluated from a single-medium (surface water) perspective using a subset of the scoring elements. The results of the latter process have been used in the development of an effluent monitoring priority pollutants list for Ontario's Municipal/Industrial Strategy for Abatement (MISA) initiative, the aim of which is the virtual elimination of toxic chemicals from Ontario waters.

TABLE 1: SCORING SYSTEM ELEMENTS

Phase 1

This phase identifies chemicals of potential concern. Information from the open literature, chemical lists developed by recognized agencies that have regulatory and assessment responsibilities, and monitoring surveys are reviewed.

Phase 2

Preliminary Assessment

a) Elements describing exposure

- P2E1 - Sources
- P2E2 - Releases
- P2E3 - Environmental Distribution
- P2E4 - Environmental Transport
- P2E5 - Environmental Persistence
- P2E6 - Bioaccumulation

b) Elements describing adverse effects (toxicity)

- P2E7 - Acute Lethality
- P2E8 - Other Toxicity

c) Element describing undesirable aesthetic effects

- P2E9 - Undesirable Aesthetic Effects

Phase 3

Detailed Assessment

a) Elements describing exposure

- P3E1 - Environmental Concentrations - Air
- P3E2 - Environmental Concentrations - Water
- P3E3 - Environmental Concentrations - Soil
- P3E4 - Environmental Concentrations - Sediment
- P3E5 - Environmental Concentrations - Animals
- P3E6 - Environmental Concentrations - Plants

b) Elements describing adverse effects (toxicity)

- P3E7 - Acute Lethality
- P3E8 - Sublethal Effects on Non-mammalian Animals
- P3E9 - Sublethal Effects on Plants
- P3E10 - Sublethal Effects on Mammals
- P3E11 - Teratogenicity
- P3E12 - Genotoxicity/Mutagenicity
- P3E13 - Carcinogenicity

c) Element describing undesirable aesthetic effects

- P3E14 - Undesirable Aesthetic Effects

SCORING CRITERIA FOR PHASE 2 VECTOR ELEMENTS

ELEMENT NUMBER	UNITS	SCORING CRITERIA			
		0	1	2	3
P2E1	kg/yr	<5	5 to 300	300 to 10000	>10000
P2E2	% release narrative	0 not used or imported in Ontario	0 to 3 used in closed systems with no routine releases	>3 to 30 Most converted to another product, OR OR largely restricted to industrial uses, OR very slowly released, OR shipped in large batches	>30 Most released directly into the environment, OR used in an open, dispersive manner
P2E3	Measurement basis	Not yet detected in Ontario	Infrequently detected at specific locations	Frequently detected but only at specific sites	Frequently detected over much of Ontario
	Release basis	No known release sites in Ontario	Few release sites concentrated in a few locations	Relatively few release sites, but not concentrated in a few locations	Many release sites throughout Ontario
P2E4	narrative	<5% of releases partitions into other media	≥ one media other than receiving medium containing 5-10% of the amount released	≥ one medium other than the receiving medium containing 10-20% of the amount released	> two media other than receiving medium containing more than 20% of the amount released, OR most is associated with fine particles when released into the environment
P2E5	t 1/2 (days) narrative	<10 designated not persistent	10 to <50 slightly persistent	50 to <100 moderately persistent	>100 very persistent
P2E6	BCF Log K _{ow}	≤20 ≤2.0	>20 to 500 >2.0 to 4.0	500 to 15000 >4.0 to 6.0	>15000 >6.0
P2E7	Oral LD ₅₀ mg/kg	>5000	>500 to 5000	50 to 500	<50
	Dermal LD ₅₀ mg/kg	>5000	>500 to 5000	50 to 500	<50
	Inh LC ₅₀ mg/M	>15000	>1500 to 15000	150 to 1500	<150
	Aquatic LC ₅₀ mg/L	>1000	>100 to 1000	10 to 100	<10

SCORING CRITERIA FOR PHASE 2 VECTOR ELEMENTS

ELEMENT NUMBER	UNITS	SCORING CRITERIA			
		0	1	2	3
P2E8	Narrative	No evidence of chronic effects in more than one species	Evidence of chronic effects not detrimental to the continued development and well-being of the test system	Evidence of chronic adverse effects in one species but negative data in another species	Evidence of chronic effects in more than one species
P2E9	water				
	mg/L	No effects	>10	0.01 to 10	<0.01
	air				
	ppm	No effects	>10	0.01 to 10	<0.01

SCORING CRITERIA FOR PHASE 3 VECTOR ELEMENTS

ELEMENT NUMBER ^a	Units	0	2	4	6	8	10
P3E1	ug/M ³	<0.03	>0.03-0.3	>0.3-3	>3-30	>30-300	>300
P3E2	ug/L	<0.3	>0.3-3	>3-30	>30-300	>300-3000	>300
P3E3	ug/kg with						
	K _{OW} <1	<0.6	≥0.6-6	>6-60	>60-600	>600-6000	>6000
	K _{OW} 1-3	<6	≥6-60	>60-600	>600-6000	>6000-60000	>60000
	K _{OW} 3-5	<60	≥60-600	>600-6000	>6000-60000	>60000-600000	>600000
	K _{OW} >5	>600	≥600-6000	>6000-60000	>60000-600000	>600000-6000000	>6000000
P3E4	ug/kg	>5	≥5-50	>50-500	>500-5000	>5000-50000	>50000
P3E5	ug/kg	<0.6	≥0.6-6	>6-60	>60-600	>600-6000	>6000
P3E6	ug/kg	<0.6	≥0.6-6	>6-60	>60-600	>600-6000	>6000

SCORING CRITERIA FOR PHASE 3 VECTOR ELEMENTS

ELEMENT NUMBER	Units	0	2	4	6	8	10
P3E7	oral LD ₅₀ mg/kg	>5000	>500-5000	>50-500	>5-50	>0.5-5	≤0.5
	dermal LD ₅₀ mg/kg	>5000	>500-5000	>50-500	>5-50	>0.5-5	≤0.5
	inhalation LC ₅₀ mg/m ³	>15000	>1500-15000	>150-1500	>15-150	>1.5-15	≤1.5
	aquatic LC ₅₀ mg/L	>1000	>100-1000	>10-100	>1-10	>0.1-1	≤0.1
P3E8	aquatic non-mammals - EC ₅₀ , mg/L	≥20	>20-2	>2-0.2	>0.2-0.02	≤0.02	≤0.02
	MATC, mg/L	≥2	>2-0.2	>0.2-2	>0.02-0.002	≤0.002	≤0.002
	NOAEC, mg/L	≥0.2	>0.2-0.02	>0.02-0.002	>0.002-0.0002	≤0.0002	≤0.0002
						in one genus	in different genera
	terrestrial non-mammals - sub-chronic NOEL, mg/kg	≥1000	>100-1000	>10-100	>1-10	≥1	≥1
	chronic NOEL, mg/kg	≥500	>50-500	>5-50	>0.5-5	≥0.5 in one genus	≥0.5 in different genera

SCORING CRITERIA FOR PHASE 3 VECTOR ELEMENTS

ELEMENT	NUMBER	Units	sub-lethal effects on plants	aquatic species	EC ₅₀ , mg/L	HQAC, mg/L	EC ₅₀ mg/L water	mg/m ³ air	mg/kg soil	HQAC	mg/L water	mg/m ³ air	mg/kg soil	OR	measurable effects	Reversible effects such as induction and sub-cellular effects	Reversible effects, not dysfunctional	Reversible degenerative effects, slightly dysfunctional	Reversible pathological effects	Irreversible pathological effects
	0		>10-100	>10	>10	>100	>10000	>10000	>100-1000	>10-100	>1000-10000	>1000-10000	>10-100	>100	no effects	effects	effects	effects	effects	effects
	2		>1-10	>1-10	>1-10	>1-10	>1-10	>1-10	>100-1000	>1-10	>100-1000	>100-1000	>10-100	>1-10	effects such as induction and sub-cellular effects	effects, not dysfunctional	Reversible effects, slightly dysfunctional	Reversible pathological effects	Reversible pathological effects	Irreversible pathological effects
	4		>1-10	>1-10	>1-10	>1-10	>1-10	>1-10	>100-1000	>1-10	>100-1000	>100-1000	>10-100	>1-10	effects such as induction and sub-cellular effects	effects, not dysfunctional	Reversible effects, slightly dysfunctional	Reversible pathological effects	Reversible pathological effects	Irreversible pathological effects
	6		>1-10	>1-10	>1-10	>1-10	>1-10	>1-10	>100-1000	>1-10	>100-1000	>100-1000	>10-100	>1-10	effects such as induction and sub-cellular effects	effects, not dysfunctional	Reversible effects, slightly dysfunctional	Reversible pathological effects	Reversible pathological effects	Irreversible pathological effects
	8		>1-10	>1-10	>1-10	>1-10	>1-10	>1-10	>100-1000	>1-10	>100-1000	>100-1000	>10-100	>1-10	effects such as induction and sub-cellular effects	effects, not dysfunctional	Reversible effects, slightly dysfunctional	Reversible pathological effects	Reversible pathological effects	Irreversible pathological effects
	10		>1-10	>1-10	>1-10	>1-10	>1-10	>1-10	>100-1000	>1-10	>100-1000	>100-1000	>10-100	>1-10	effects such as induction and sub-cellular effects	effects, not dysfunctional	Reversible effects, slightly dysfunctional	Reversible pathological effects	Reversible pathological effects	Irreversible pathological effects

P3E9

SCORING CRITERIA FOR PHASE 3 VECTOR ELEMENTS

ELEMENT NUMBER	Units	0	2	4	6	8	10
P3E10	sub-lethal effects on mammals - oral NOEL mg/kg ihl NOEL mg/m ³	>1000 >3000	>100-1000 >300-3000	>10-100 >30-300	>1-10 >3-30	>0.1-1 >0.3-3	<0.1 <0.3
P3E11	narrative mg/kg	No terata at >1000	Terata or developmental anomalies at >50-1000	Terata or developmental anomalies at >10-50	Terata or developmental anomalies at >1-10	Terata at >0.1-10	Terata at ≤0.1
P3E12	narrative	No evidence of genotox. or mutagen. with adequate testing	Positive results in <u>in vitro</u> only	Genotox./mutagen. in prokaryotic systems only	Effects on DNA, but no direct DNA interactions	Clastogenic effects but no direct interactions with DNA	Genotoxic/mutagenic usually with direct interactions with DNA

SCORING CRITERIA FOR PHASE 3 VECTOR ELEMENTS

ELEMENT NUMBER	Units	0	2	4	6	8	10
P3E13	narrative	No tumours in adequate studies, and does not interact with genetic material	Tumours in one species, and negative in others, and does not interact with genetic material	Tumours in more than one species, and does not interact with genetic material	Tumours in bioassays at doses causing metabolic saturation, or associated with lesions that pre-dispose to tumours. No interaction with DNA	Indirect acting carcinogen, no interaction with genetic material	Direct acting carcinogen that interacts with genetic material
a.	P3E1	Concentrations in air					
	P3E2	Concentrations in water					
	P3E3	Concentrations in soils					
	P3E4	Concentrations in sediments					
	P3E5	Concentrations in plants					
	P3E6	Concentrations in animals					
	P3E7	Acute lethality					
	P3E8	Sub-lethal effects on non-mammalian species					
	P3E9	Sub-lethal effects on plants					
	P3E10	Sub-lethal effects on mammals					
	P3E11	Teratogenicity					
	P3E12	Genotoxicity/Mutagenicity					
	P3E13	Carcinogenicity					
	P3E14	Undesirable aesthetic properties					

APPENDIX B COMBINING RULES

1. Flow Diagram for Phase 2 Combining Rules

Rule	List Assignment
P2R1 Is P2E9 ≥ 1 -----> YES -----	>P2L4 undesirable aesthetic effects
NO	
P2R2 Is P2E7 or P2E8 = 3? -----> YES -----	>P2L1 high priority for P3 assessment
NO	
P2R3 Are there ≥ 4 "*" scores for P2E1 through P2E6 OR Do P2E7 and P2E8 have "*" scores? -----> YES -----	>P2L5 insufficient data
NO	
P2R4 Is the sum of the highest scores for two of elements P2E1 through P2E6 plus the highest score for elements P2E7 or P2E8 > 4 and the highest score for P2E7 or P2E8 not = 0? -----> YES -----	>P2L2 intermediate priority
NO -----> P2L3	low priority
P2R5 Is the sum of the highest scores for two of elements P2E1 through P2E6 plus the highest score of elements P2E7 or P2E8 ≥ 6 and not = 0? -----> YES -----	>P2L1 high priority for P3 assessment
NO -----> P2L2	intermediate priority

2. Flow Diagram for Phase 3 Combining Rules

Rule	List Assignment
P3R1 Are any scores of elements P3E7 through P3E13 ≥ 8 and any of elements P3E1 through P3E6 > 0 ? -----> YES -----	>P3L1 high priority for detailed study
NO	
P3R2 Are there ≥ 6 "*" scores for elements P3E1 through P3E6 or P3E7 through P3E13? -----> YES -----	>P3L5 insufficient data
NO	
P3R3 Are the two highest scores for elements P3E1 through P3E6 plus the two highest scores for elements P3E7 through P3E13 ≥ 24 ? -----> YES -----	>P3L1 high priority for detailed study
NO	
P3R4 Are the two highest scores for elements P3E1 through P3E6 plus the two highest scores for elements P3E7 through P3E13 ≥ 14 ? -----> YES -----	>P3L2 intermediate priority
NO -----> P3L3	low priority
P3R5 Is the chemical on Phase 2 list P2L4? -----> NO -----	>No action
YES	
Has the chemical been screened for regulatory assessment? -----> YES -----	>No action
NO -----> P3L4	undesirable aesthetic effects

RECEPTOR MODELLING OF AMBIENT PARTICULATES AT EAST RIVERDALE AND AT TORONTO CONTROL SITES

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Abstract

Further research has continued during 1987 into the capabilities of statistical factor analysis and chemical element balance to identify individual emission sources and to determine their respective contributions at a particular site. Airborne particulate matter collected using both hi-vol samplers and cascade impactors at several Metro Toronto sites, including an E. Riverdale location, analyzed by radioanalytical IPAA and INAA, were subjected to receptor modelling (i) as size fractionated and (ii) as total particle collections to differentiate sources having similar concentration 'profiles' but different particle-size profiles. A more thorough hi-vol and impactor air sampling program has been initiated in a downwind area to further investigate waste incinerator impacts in urban airsheds. For reference, hi-vol air samples were obtained since January at Queen's Park and multi-elemental analysis performed using INAA to identify 3 major sources and their contributions with the aid of statistical factor analysis and chemical element balance.

Introduction

Atmospheric research done during 1987 in our laboratory in the University of Toronto and supported recently by the Ministry has concerned the developing of ways to deduce the identity of contributing air particulate emission sources at urban receptor sites and estimating their relative contributions. Emphasis has been placed on obtaining multielemental composition data for ambient aerosol that is sufficiently extensive and accurate to permit validation of existing receptor models in a Canadian environment and possible improvement through modification of models. The objective of a suitable receptor model is to provide a means to represent a set of aerosol concentrations as sampled at particular locations in terms of the respective contributions of a finite set of emission sources which are characterized by certain distinctive identifying features such as inter-elemental concentration patterns or source

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profiles'. Previous research in this and other environmental groups has established that such characteristic trace elemental patterns exist for sources such as combustion and incineration plants, ferrous and non-ferrous industry, motor vehicles, soil dust, etc.

This receptor approach to assessing levels of air pollution from known sources and their relative environmental and public health significance thus focusses attention on the composite nature and fluctuating ambient concentrations of various airborne constituents at the site where they impact and, this information can be more directly applied to public health hazard assessment than alternate dispersion model approaches based on source emission inventories used to compute impacts at various locations of interest.

For this research, radioanalytical methods (neutron plus photon activation) have been applied to air particulate samples obtained in the greater Toronto region using Hi-Vol samplers and 6-stage Sierra impactors. Results reported previously (1,2) demonstrated that 5-6 sources could be clearly resolved in such urban atmospheres through statistical factor analysis performed on data sets of 18-25 repeat samplings both at an industrial site and a suburban site (light industry/residential). By inputting source concentration profiles into a chemical element balance (CEB) computation, it was possible to deduce the relative contributions at these sites:

industrial (E. Riverdale): soil(1%), motor vehicles(25%), non-ferrous industry(46%), incinerators(28%)

suburban (Port Credit): soil(69%), motor vehicles(8%), incinerators(6%), road salt(13%), glass factories(3%), oil(1%)

However, at the former site, distinctive sources having similar concentration profiles but different particle size distributions could only be distinguished by application of a new size-specific elemental mass balance model or SSEMB, whereas such an approach had not been necessary in the less complex atmosphere of the suburban location. The current study reports attempts to model at a central (Queen's Park) site and to compare modelling of single Hi-Vol samples with size-sorted samples at the E. Riverdale site.

Methods

Air particulate samples were collected using a standard hi-vol sampler at regular intervals during the period between April and June, 1987 at Queen's Park. This sampling location represented a typical urban site with a huge traffic volume. The sampler was operated at a flow rate of about 1 m³/min for 10 hour periods, and the total collected air volume was about 600 m³. Whatman

#41 filter sheet was employed to collect the air particulate because of its low trace element content (3,4). Glass fibre, a standard hi-vol filter medium, is extremely unsuitable for instrumental neutron activation analysis because of its high sodium and ash content.

In order to take advantage of particle size distributions unique to different emission sources, ambient aerosols sampled at the E. Riverdale MOE site were size-sorted using a 6-stage Sierra 235 cascade impactor capable of operating up to a maximum flow-rate of $1.1 \text{ m}^3 \cdot \text{min}^{-1}$ which permitted total collections of 1600 m^3 . Whatman 41 which had been lightly impregnated with vase-line was used as interstage collection surfaces. In some measurements published recently (1,2,5), the ability of the Sierra 235 faithfully to separate air particulate matter into six fractions with effective aerodynamic cut-off diameters of >7.2 , 4.2 , 1.8 , 0.7 , 0.35 and <0.2 microns, respectively, was demonstrated. For multielemental trace analysis, the loaded filters were cut into four sections of equal area and the edges trimmed to avoid contamination from handling and any contact from the filter cartridge. Two sections were placed into two 7 cm^3 acid pre-washed polyethylene capsules, separately and subjected to thermal neutron activation analysis (INAA) at the University of Toronto SLOWPOKE-2 nuclear reactor. The filters were irradiated under neutron flux ranging from 1 to $2.5 \times 10^{11} \text{ n/cm}^2 \cdot \text{s}$ for periods from 5 minutes to 16 hours. The elemental concentrations of Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na, Ti were analyzed using their short-lived nuclides, while the concentrations of As, Ag, Ce, Co, Cr, Cs, Eu, Hf, K, La, Sb, Sc, Sm, W and Zn were found using their long-lived nuclides. Photon activation was performed on filter segments using the NRC (Ottawa) linear accelerator for determination of Pb, Ti and Zr. Radioactive filter samples were counted using a gamma-ray spectrometer which consisted of a 93 cm^3 Aptec Ge detector of 21.6% efficiency relative to NaI and resolution of 1.90 keV FWHM at 1.33 MeV, in conjunction with a TRACOR Northern TN 4000 pulse-height analyzer. All the results were computed using the comparator method employing a U.S. National Bureau of Standards (NBS) reference material, SRM 1632a, as the multielement standard. However, Cu standards had to be prepared separately for the analysis because SRM 1632a did not provide sufficient copper to give an accurate determination of the concentration of that element.

Results and Discussion

The average concentrations of all the chemical elements measured in the air particulate matter at Queen's Park are given in Table 1. Also presented are results obtained from the E. Riverdale (industrial) site in 1986.

Table 1
Elemental Concentrations in Airborne Particulate Matter (ng/m³)

Element	Queen's Park 1987	Eastern Ave. 1986 (2)
Al	2500 (620-8100)	1580
Ag	2.8 (0.78-7.4)	----
As	1.6 (0.1-3.3)	6.5
Br	40 (23-62)	73.7
Ca	7800 (1800-13000)	6100
Ce	>2.7 (0.5-7.5)	>1.5
Cl	2100 (960-3100)	4400
Co	0.75 (0.3-1.5)	0.8
Cr	9.7 (4.6-17)	15
Cs	>0.12 (0-0.28)	>0.2
Cu	1500 (780-1900)	110
Eu	0.06 (0.03-0.09)	0.14
Fe	2000 (690-3700)	2100
Hf	>0.31 (0-1.4)	>0.2
I	2.2 (0.9-3.5)	>20
K	800 (190-2400)	500
La	1.5 (0.3-4.7)	1.2
Mg	870 (310-1900)	----
Mn	100 (36-250)	72
Na	890 (570-1400)	990
Sb	2.2 (0.77-4.0)	14.4
Sc	0.34 (0.08-0.69)	0.3
Se	>1.9 (0.6-4.6)	>1.7
Sm	0.24 (0.04-0.7)	0.1
Ti	250 (66-570)	140
V	8.2 (2.5-28)	5.5
W	>0.41 (0-0.71)	>0.6
Zn	120 (63-190)	470

The concentration of Cu in the aerosol found in this study was more than 10 times higher than that obtained at the industrial site. The unusual high concentration and low community of Cu suggests that there might be a source contributing Cu alone in the aerosol. A possible explanation is the mechanical erosion of the brushes on the sampler motor. Also, the concentrat-

ions of Mn and Br measured show that there is a trend towards higher concentration of Mn and lower concentration of Br in the aerosol during recent years. Since Br is a 'key marker' element for the burning of leaded gasoline, the decrease in its concentration indicates that the consumption of leaded gasoline has decreased. As more vehicles have switched to operate on unleaded gasoline, an increase in the level of Mn, an octane-boosting substituent (MMT), in the atmosphere is not surprising.

In order to identify the possible sources contributing at the (Queen's Park) receptor site, the data set of all the elements measured in the air particulate collected was subjected to factor analysis. However, the resulting factor pattern was very difficult to interpret and included many elements with low communities, such as Cu. Since the low communities might be an indication of the elements being poorly correlated with other elements in the data set, or simply an analytical error, several elements were eliminated, and the analysis was carried out using the remaining 15 elements. Table 2 presents a three factor solution which can easily be interpreted.

Table 2
Factor Pattern for the Queen's Park Aerosol (Factor loadings)

Soil	Oil/Coal Combustion	High Temperature Combustion
La (0.97)	V (0.82)	Sb (0.88)
K (0.96)	Cr (0.69)	Zn (0.81)
Al (0.94)	Co (0.67)	
Ce (0.91)	Sc (0.65)	
Mn (0.91)	Fe (0.61)	
Ti (0.89)		
Ca (0.79)		
Fe (0.75)		
Sc (0.72)		

Factor one shows a strong correlation among elements such as Al, La, K and Ca, which are all associated with lithophilic sources. These elements could be originated from a combination of construction and traffic activities. The sampling station is close to a major intersection (University and College) with a traffic volume of over 600,000 vehicles a day (6). As a result, the concentrations of crustal elements in the aerosol are higher than those measured at the E. Riverdale site.

Factor two is correlated with elements such as V, Co and Cr, which are

often associated with oil and coal combustion. Co and Cr are mainly associated with coal combustion which exhibits a composition 'profile' very similar to that of the lithophilic elements. It was observed from the interelement correlations in the factor analysis that Cr correlates fairly well with other crustal elements. On the contrary, the weak correlation between Co and the crustal elements might indicate that the major contribution of Co would be from anthropogenic sources. V, as is well documented (4,7,8,9) is always a 'key marker' element for oil combustion.

Factor three is associated with Zn and Sb which could be considered to represent non-ferrous high temperature combustion, possibly refuse incineration (10,11,12). The lack of lithophilic association in this factor indicates that fossil fuel and soil contributions are not important. Such particles usually possess particle-size profiles which consist primarily of fine, submicron particles. Table 1 indicates that the concentrations of Zn and Sb measured at Queen's Park are lower than those at the E. Riverdale site. It might be explained by the fact that less high temperature combustion activities such as refuse and sewage incineration, are located in the vicinity.

In order to quantitatively apportion the aerosol among the three sources deduced by factor analysis, a chemical element balance will be applied to the aerosol data. The three source profiles used in the chemical element balance are taken from a compilation of literature data (2,4,13,14) and are listed in Table 3.

Table 3
Chemical Element Balance Source Profile ($\mu\text{g/g}$)

Element	Soil	Oil/Coal Combustion	High Temperature Combustion
Al	50000	4700	14000
Ca	109100	26000	17000
Ce	67	42	12
Co	10	5	20
Cr	65	580	490
Fe	30000	14000	6500
K	10600	1300	0
La	52	49	2.8
Mn	650	300	730
Sb	0.6	221	1600
Sc	10	0.6	1
Ti	3600	77	1800
V	73	12200	31
Zn	490	730	120000

In order to assess the need to have used an impactor sampler and the size-specific elemental mass balance model (SSEMB) to compute relative source contributions in the more complex airshed at the industrial site, and considering that most agencies do not use 5 or 6 stage air samplers, some calculations were done using the stage-by-stage elemental concentration data to compare the results of applying regular (single stage) Hi-Vol sampling and impactor sampling. The results obtained previously (1985-86) at E. Riverdale by use of the 6 stage Sierra and stage-by-stage trace analysis were summed for each element to yield (a) elemental concentrations and (b) estimates of total suspended particulate (TSP), as if all sampling had been done instead with a standard, single stage Hi-Vol. Modelling by chemical element balance for the six factors is compared to the results of applying SSEMB to the size-sorted samples in table 4. These results are shown both for TSP and for an important element in that region that has multiple sources, lead.

Table 4
TSP and Lead Apportionment Predicted by the CEB and SSEMB

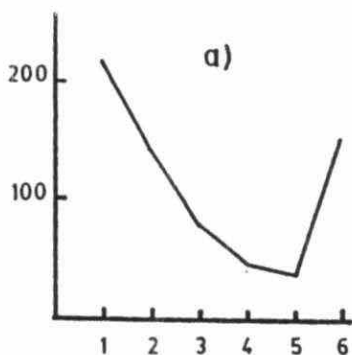
Source	TSP (%)		Airborne Lead (%)	
	SSEMB	CEB	SSEMB	CEB
Soil and Dust	74.4	73.9	9.0	9.7
Vehicle Emissions	6.4	13.1	20.6	46.2
Lead Refining	14.5	7.5	68.2	39.6
Incineration	0.4	0.7	1.1	2.1
Casting Plant	1.9	3.5	1.6	3.4
De-icing Salt	2.4	1.3	0	0

It can be seen that fair agreement is obtained for dominant source contributions such as wind-entrained soil and surface dust, but the CMB results are in poor agreement for sources which have significant contributions from some elements of different particle sizes, e.g. Pb from non-ferrous refining and casting and from motor vehicles, Zn and Mn. Similarly, the results of predicting the size distributions of Pb concentrations by CEB compared to SSEMB are shown in the figure and it is seen that the SSEMB predictions are quite good over the size range from >7 to <0.2 microns of the 6 impactor stages whereas the CMB-predicted concentrations are strongly biased to the submicron range.

Finally, as an independent test of the goodness of fit of the receptor models at the industrial site, the elemental predicted/measured ratios, as L/S, larger/smaller ratios are given in table 5. The predictions of SSEMB/TOTAL agree much better than the other predictions and the L/S ratio average of 2.2 obtained is considered to be quite good among receptor models being assessed at present here and elsewhere. These comparisons clearly demonstrate that SSEMB is absolutely essential when colinear sources are important.

Table 5
Larger/Smaller Ratios for CEB and SSEMB Predictions

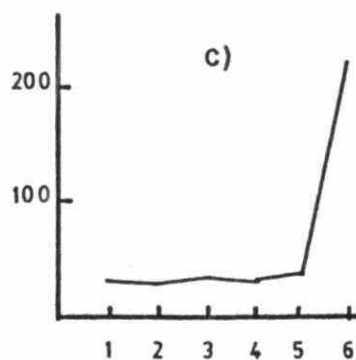
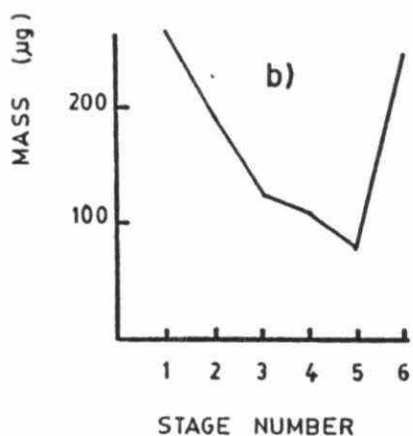
Element	SSEMB/Total	CEB	SSEMB
Al	1.21	2.16	1.46
As	2.04	1.9	2.6
Br	1.15	1.21	1.3
Ca	2.03	3.95	2.00
Ce	1.59	2.66	2.0
Co	2.79	5.06	4.69
Cr	3.35	6.1	4.24
Cs	4.76	7.0	10.9
Eu	4.99	8.0	15.0
Fe	1.35	2.2	1.53
K	2.45	2.15	1.81
La	1.37	2.51	2.3
Mg	2.55	4.16	2.82
Mn	2.37	3.4	2.7
Na	1.14	1.11	1.67
Pb	1.48	2.35	1.65
Sb	1.16	1.11	1.4
Sc	1.29	2.29	1.61
Sm	2.81	2.06	2.4
Th	1.6	2.47	2.04
Ti	1.9	3.5	2.29
V	3.25	5.1	6.34
Zn	1.25	1.23	1.81
Average	2.17	3.07	3.2



a) SSEMB

b) OBSERVED

c) CMB



OBSERVED AND PREDICTED SIZE DISTRIBUTIONS
FOR AIRBORNE LEAD

Conclusions

Receptor modelling can be useful both for identifying contributing emission sources and for computing their relative contributions at given sites. Such calculations performed on a data set of hi-vol filters from a general urban site are possible provided sufficiently extensive sampling and analysis is performed. However, at more complex industrial sites, it appears necessary to make use of the particle size distribution information and a modified form of model, such as the SSEMB.

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**Development of Multivariate Analysis Procedures
for Ontario Air Quality Data**

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Abstract

The objective of this project is to examine the use of advanced pattern recognition methods and multivariate statistical procedures for maximal extraction of information regarding origins, transport, and deposition of airborne pollutants in Ontario. The initial phase of the project is focusing on the Event Wet/Dry Deposition Network data obtained by the Acidic Precipitation in Ontario Study (APIOS). Two types of eigenvector studies will be initially tested; principal components analysis incorporating back trajectory calculations, and three-mode factor analysis. By coding the endpoint geographical region of the back trajectory as an additional variable, it is anticipated that the components analysis may provide additional insights into the origin and transport of the measured species. Three-mode factor analysis is a relatively unknown method for simultaneously looking at the spatial and temporal variations in a multivariate data set. It is a model that explicitly allows the use of multilocation data over time and it is again anticipated that it will provide new insights into the interrelationships that govern the pattern of species deposition as measured by the APIOS network.

Introduction

The accumulation of analytical data characterizing environmental systems is only the first step in the elucidation of information needed for understanding the functioning of such systems and the development of effective management strategies. Improvements in sampling and multiple species analytical methods now permit large data sets to be obtained. Since the environment is a complex multivariate system, it is essential that multivariate data analysis methods be developed and employed to extract the maximum amount of information from a data set. Environment Ontario is currently collecting several large data sets characterizing airborne particle and precipitation composition throughout lower Ontario. The purpose of our project is to explore the use of a variety of multivariate statistical methods and provide a data analysis scheme for maximizing the use of such data in the future. The initial efforts are focusing on the incorporation of back trajectory information into the analyses and the use of a novel form of factor analysis, three-mode factor analysis, for analyzing the spatial and temporal variations in the data from the Event Network of the Acidic Precipitation in Ontario Study (APIOS).

Incorporation of Back Trajectory Information

The application of eigenvector analysis to precipitation or particle compositional data can identify the measured species that covary in the system. Usually this covariance is due to the impact of a particular source type. For example, lead and bromine covary because they are both emitted from automobiles that burn leaded gasoline. However, the covariance can also arise from meteorological influences. For example in Houston,

Texas, there is a strong negative correlation between chlorine and sulfur in airborne particles. This correlation occurs because when the wind blows on-shore from the Gulf of Mexico, there is high sea salt chlorine and low anthropogenic sulfur. When the wind blows off-shore there is an increase in sulfur from coal-fired power plants and other industrial activities and a sharp decrease in the marine contribution.

For regional scale receptor modeling the influence of meteorology becomes greater and to separate the influence of the different surrounding areas on a receptor site, it is necessary to incorporate meteorological data into the calculation. An interesting approach to adding such information has been presented by Malm et al. (1986). For each sample back trajectories are calculated. The region surrounding the receptor site is divided into subregions. A new variable is defined as the number of time segments the back trajectory calculations shown are in each of the defined subregions. Malm et al. (1986) have examined the sources of visibility degradation at the Grand Canyon with considerable success using this approach. We are currently in the process of analyzing the three hour back trajectory results obtained using the approach described by Yap and Kurtz (1986). The results of this study should permit us to determine the utility of this approach.

Three-Mode Factor Analysis

Introduction

Factor and principal components analysis have been widely used in elucidating the interrelationships within a multivariate data set (Hopke, 1985). Environmental systems are typically characterized by taking

samples over time at a number of sampling sites. These samples are then characterized by a variety of analytical methods so that the data set can be represented by a data cube as illustrated in Figure 1. Such a data set provides information on the simultaneous temporal and spatial variation in the system. However, the conventional components analysis methods are really designed to analyze the data rectangle obtained by taking a slice of the cube in one of the three orthogonal directions. For factor and principal components analysis this slice is typically the measured concentrations at a single location over time.

The empirical orthogonal function approach analyzes a single species concentration over sites and time (Peterson, 1970). One can perform a spatial analysis of elemental concentrations over sites for a single time interval. However, each of these methods is only looking at a single plane in the data cube. A different factor analysis approach is needed that offers the opportunity to simultaneously examine the spatial and temporal variations in the data and thus potentially infer more information about the origins and transport of observed atmospheric species. This method is called three-mode factor analysis (Kroonenberg, 1983).

Principles

To understand three-mode factor analysis, it may be helpful to first review standard principal components analysis as obtained using a singular value decomposition. A principal components analysis is really a combination of two of the three matrices derived with a singular value decomposition as shown in Figure 2. Thus, we can consider that the G matrix holds information on the idealized samples while the H matrix holds information

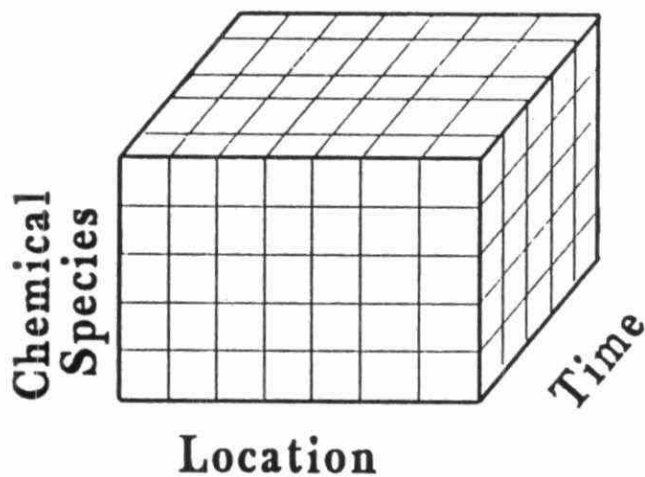


Figure 1. Schematic representation of environmental compositional data taken at various sites over time.

Data

Time Periods
1...j...m

Species
Concentration
1...i...l

Z

6

Singular Value Decomposition

Time Periods
1...j...m

Species
Concentration
1...i...l

G

1...p...s

C

1...q...t

H'

Standard

PCA

Q-Mode

1...i...l

A

Scores

t Sources

1...q...t

H'

Loadings

1...p...s

G

Loadings

s Idealized Samples

1...j...m

B'

Scores

Figure 2. Review of the singular value decomposition in principal component analysis.

on the time periods. The multiplication of the core matrix by one or the other matrix permits the extraction of the information in the form of factor loadings that need to be interpreted as the new variables in the system. As described above, in standard factor analysis, the columns of the loading matrix are interpreted as being the effects of the sources observed in the airshed.

Mathematically the singular volume decomposition is written as

$$Z = GCH' \quad (2)$$

$$z_{ij} = \sum_{p=1}^s \sum_{q=1}^t g_{ip} h_{jq} c_{pq} \quad (3)$$

If $A = GC$ and $H' = F$, then

$$Z = AF \quad (4)$$

yielding the form of equation 2 for each individual datum point.

The idea can then be extended to the three dimensions of space, time, and composition as outlined in Figure 3. The core matrix now has three modes and does not have the simple relationship to the loadings as in the two dimensional case. We now have a model of the form

$$z_{ijk} = \sum_{p=1}^s \sum_{q=1}^t \sum_{r=1}^u g_{ip} h_{jq} e_{kr} c_{pqr} \quad (5)$$

In the two dimensional case, the core matrix is diagonal while in the three-mode case, it is generally not and thus the multiple interactions between time, location, and composition can be explored with the sum of the square of the elements of C being the total sum of squares of the three-mode model to the original data.

Three-mode analysis has had only limited applications and primarily in the area of educational psychology. There are two reports of application

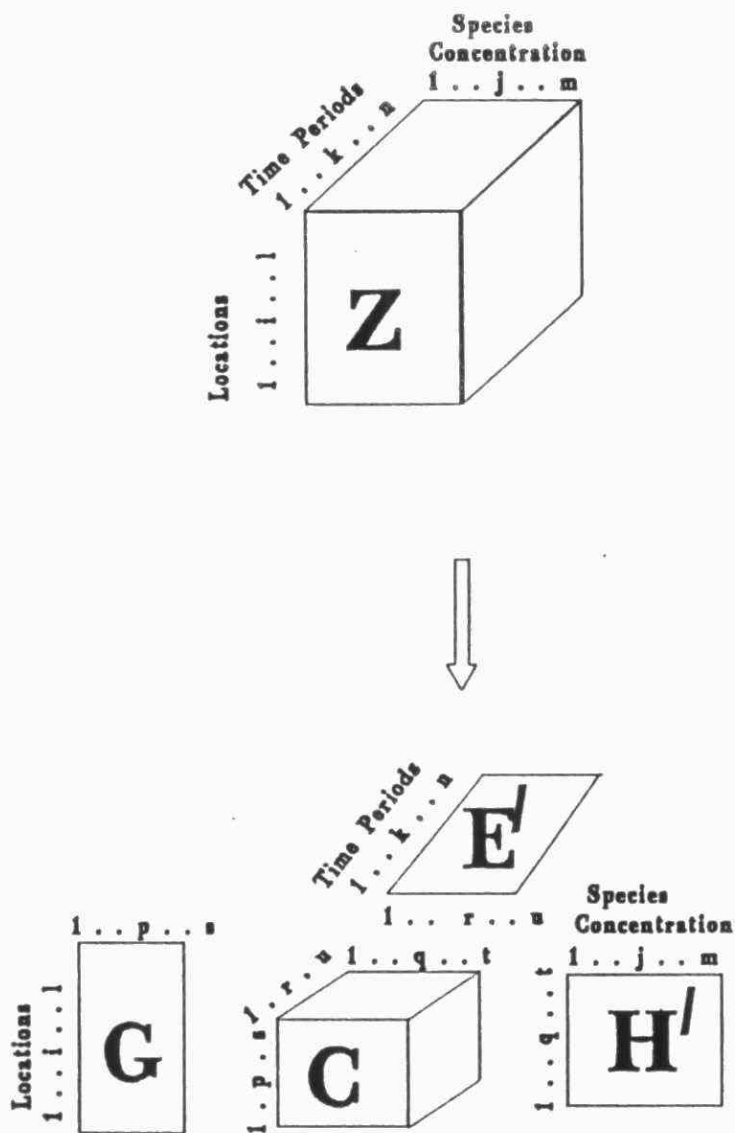


Figure 3. Outline of three-mode principal components model.

to geological problems (Hohn, 1979; Hohn and Friberg, 1979). Thus, an initial exploration of this technique will be needed. The programs implementing several computational methods to perform such analyses are available in the University of Illinois' statistical package SOUPAC and from programs obtained from Dr. Kroonenberg.

If samples are collected at different positions in different time periods, and some properties (typically chemical species) are determined for the samples, then the collected data may have three modes: time, position, and composition.

It is attractive to inspect the relations of chemical species and particulate pollution sources with respect to the variation of time and position. It is expected for the first mode (element) that we may extract several factors which correspond to particulate source mass contributions and have certain patterns relating to the patterns of the elemental emissions. Can we use the three-mode factor analysis to reveal these relations? Further, how can we apply three-mode factor analysis to the air particulate data sets and interpret the results physically?

Within the first mode (i mode), chemical species (i) and particulate source (p) are related by G_{ip} such that we may somehow specify which factor corresponds to which source in the real world, where s represents the number of sources.

The second mode is related to the positions. At this time, the physical meaning for the factors within this mode is not clear. One possible interpretation is that these factors also represent the particulate sources, then t should be equal to s and h_{jq} reflect the contribution of source q at the position j. Another possible interpretation is with the

concept of "pollution type". By this way the factors of this mode are explained as a few of pollution types or pollution zones (groups of sites impacted by the same sources). Referring to the h_{jq} values, we may assign (or classify) every position (j) into categories of pollution type.

The time period is related to meteorological conditions so that the third mode may be concluded by meteorological regimes as its factors. The core matrix (its entries are c_{pqr}) relates these factors of each mode together. The C_{pqr}^2 represents the explained variance for corresponding factor from total variance in the system.

Some matrix transformations may be needed to transform the raw matrices to achieve "simple structure" which may be more easily interpreted. It would be more attractive to find a particular transformation approach (like TTFA) to get physically meaningful and quantitative results, e.g. particulate source profile, contribution within the spatial and time series.

Preliminary Results for an Artificial Data Set

A rough initial analysis has been performed on an artificial data set. The data set has been created in the following manner. Suppose there is a source-receptor system as in the layout of Figure 4. There are two classes of sources, denoted as S1 and S2. Within a source class, the chemical composition of the emitted particles is the same. Table 1 contains the source compositions, i.e. source profiles (these data are quoted from Currie *et al.*, 1984).

Suppose the data are collected in 7 periods which have different wind direction. Based on the layout of the wind direction, the source

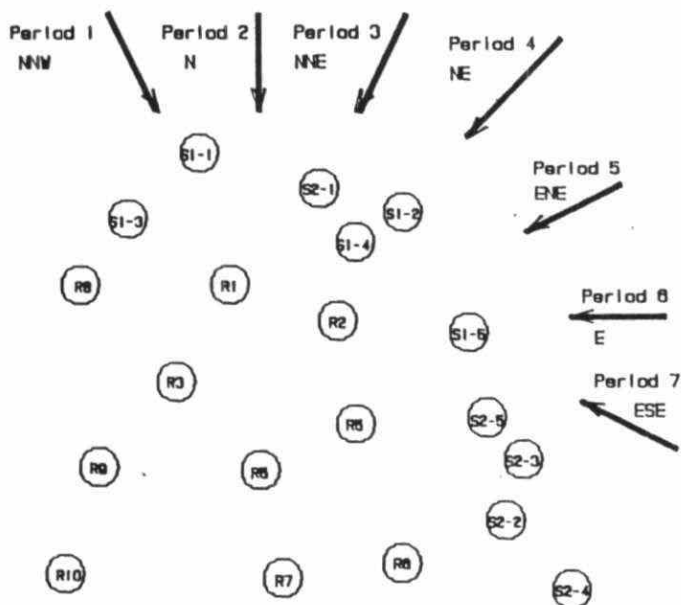


Figure 4. General configuration of sources and receptors for three-mode factor analysis test.

Table 1. Source Profile

No.	Element	S1 (Coal A)	S2 (Steel A)
1	C	30	150
2	Na	9.7	11
3	Al	26	13
4	Si	150	8
5	S	15	27
6	Cl	11	30
7	K	10	9.1
8	Ca	23	70
9	Ti	2.6	1.3
10	V	0.1	1.8
11	Cr	0.4	3.3
12	Mn	0.3	6.0
13	Fe	18	120.0
14	Ni	0.2	2.8
15	Cu	1.3	2.6
16	Zn	3.0	25
17	As	0.3	0.08
18	Br	0.2	0.1
19	Pb	2.0	7.6
20	CC*	0.1*	0.2*

*arbitrary data

contributions of each class of source (S1, S2) to 10 receptor sites are roughly built up as Table 2 using simple Gaussian dispersion modeling.

By the following equation, an artificial data set can be produced. This "observed" data set then is analyzed by three-mode method.

$$z_{ijk} = \sum_{p=1}^s x_{ip} y_{pjk}$$

where

- z_{ijk} - concentration of element i at position (sampling site) j in period k
- x_{ip} - source profile (Table 1)
- C_{pjk} - mass contribution of source p at site j in period k (Table 2)

The three-dimensional matrix created above is taken as input data to be analyzed with a three-mode principal component analysis computer program, TUCKALS3 (Kroonenberg, 1983). The three-mode model is as given in equation 5 with s , t , u set to be 2. The following are the results of this analysis.

First Mode: Element-Source. For the first mode, factor loading matrix is $G = (G_{ip})$ and is given in Table 3. It is observed that factor loadings of component 1 (G_{i1}) are consistent with source profile of source 1 (Table 1). This will be more obvious if multiply the loadings by -1, which makes the relative values of the loading similar to those of the source profile. Factor 2 has a similar relationship with source 2. The correlation coefficients between factor loadings and original source compositions are presented in Table 4.

The result has been close to the normal factor analysis when it is used as a receptor model. Therefore, it appears this mode can be used to

Table 2. Source Contribution

Period	R1		R2		R3		R4		R5		R6		R7		R8		R9		R10	
	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
1	663	10	587	23	232	5	301	11	251	5	123	5	87	0	67	0	17	0	5	0
2	782	23	630	45	350	19	335	13	287	11	131	25	133	5	368	0	38	5	31	3
3	820	103	670	43	410	69	352	13	301	12	111	60	127	11	410	5	51	5	45	5
4	750	30	553	30	453	51	321	17	332	31	89	201	88	77	383	41	121	27	89	35
5	621	43	347	45	407	63	278	63	127	79	18	612	41	333	369	89	113	198	74	222
6	437	73	187	77	137	207	89	567	27	731	0	387	5	271	297	98	73	293	21	178
7	280	203	83	139	37	263	32	783	5	653	0	289	0	187	232	110	0	278	0	59
8	622	69	437	57	289	97	244	209	190	216	67	226	70	126	304	49	59	115	38	72
9	183	62	215	37	146	91	119	301	126	303	55	206	49	127	112	45	43	126	31	84

Table 3. Factor Loading of the First Mode, G

1	element	P-1	P-2
1	C	-0.3856	-0.5780
2	Na	0.0640	0.0473
3	Al	-0.0364	0.0987
4	Si	-0.7522	0.5922
5	S	-0.0051	-0.0135
6	Cl	0.0112	-0.0438
7	K	0.0668	0.0580
8	Ca	-0.1543	-0.2004
9	Ti	0.1287	0.0694
10	V	0.1422	0.0575
11	Cr	0.1369	0.0510
12	Mn	0.1311	0.0370
13	Fe	-0.2439	-0.4718
14	Ni	0.1393	0.0528
15	Cu	0.1333	0.0580
16	Zn	0.0700	-0.0487
17	As	0.1451	0.0669
18	Br	0.1457	0.0664
19	Pb	0.1175	0.0354
20	CC	0.1460	0.0656

Table 4. Correlation Coefficients of Factor in First Mode and Source

	Source 1	Source 2
Factor 1	-0.905	-0.528
Factor 2	0.426	-0.743

recognize particulate sources from a three-dimensional data set by this method. It is expected that if a proper transformation procedure is used to transform the raw factor loading matrix (Table 3), the final factor loadings may correspond better to the sources.

Second Mode: Position-Source. The factor loadings of the second mode, i.e. $H = (h_{jq})$ are listed in Table 5. It is not clear what the factors of this mode represent, but the results are interesting. It can be observed from Table 5 that receptor sites 1, 2, 3 and 8 have the same behavior (both factor 1 and 2 have positive loading on them), and other sites have another kind of behavior (positive loading for factor 1, negative for factor 2). Referring to the system layout (Figure 5), we may divide the sites into two groups, one is primarily polluted by source 1, another by source 2, or we may say there are two kinds of pollution zones.

There is another interesting phenomenon. The variation pattern of the loadings for factor 1 is very similar to that of average mass contribution of source 1 at corresponding sites (see Table 5). If the sign is switched for the loadings of factor 2, h_{j2} , we can make the same conclusion for factor 2 and source 2. It would be fine if we can get quantitative information about the source contribution based on these phenomena by some transformation or combination with other matrix. Using these data, we may make a sketch as in Figure 6.

Third Mode: Period-Orthogonal Wind Direction. Table 6 contains the list of $E = (e_{kr})$. The projections of wind directions on direction I (factor 1) for each period are always positive while for direction II (factor 2) they varied from negative to positive. We may conclude that the wind vector in each period may be represented as a linear combination

Table 5. The Factor Loading Matrix of the Second Mode, H,
and the Average Source Contributions at Each Site

No.	Site	Factor Loading		True Source Contribution	
		Factor 1	Factor 2	Source 1	Source 2
1	R1	0.5169	0.5056	622	69
2	R2	0.3841	0.3694	437	57
3	R3	0.3106	0.0846	289	97
4	R4	0.4097	-0.3742	244	209
5	R5	0.3805	-0.4397	190	216
6	R6	0.2261	-0.3524	67	226
7	R7	0.1610	-0.1952	70	126
8	R8	0.2617	0.1854	304	49
9	R9	0.1516	-0.2424	59	115
10	R10	0.0877	-0.1095	38	72

Table 6. Factor Loading of the Third Mode, E

Period	Factor 1	Factor 2
1	0.2866	-0.2792
2	0.3665	-0.3427
3	0.4021	-0.3496
4	0.3907	-0.2641
5	0.3933	0.0379
6	0.4218	0.5133
7	0.3696	0.5897

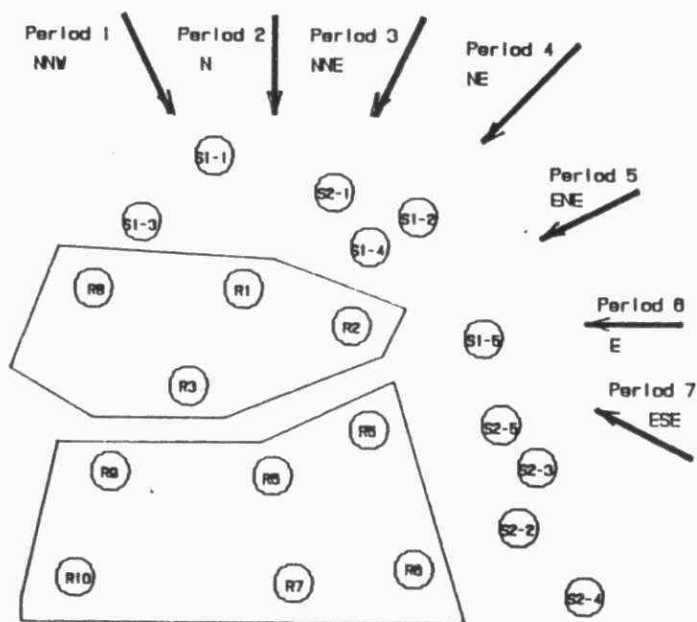


Figure 5. Partitioning of receptor sites as suggested by the second mode of the three-mode factor analysis.

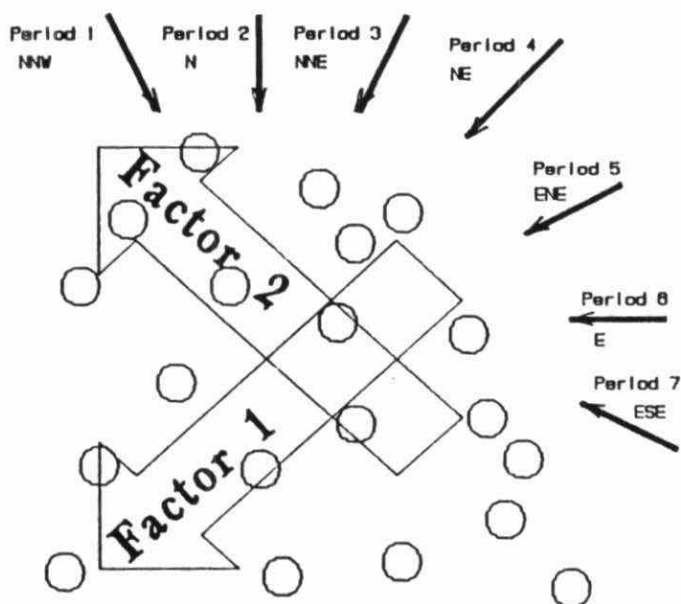


Figure 6. Directions of the two factor vectors of mode three of the three-mode factor analysis.

of primary meteorological regime (two orthogonal wind directions in this case).

Core Matrix. The core matrix C is presented in Table 7. In this table, $S1$ and $S2$ represent the two factors in the first mode (corresponding to source 1 and 2); $P1$ and $P2$ represent the two factors in the second mode (corresponding to pollution zone 1 and 2); $R1$ and $R2$ correspond to the primary wind directions, respectively.

Note that the C_{pqr}^2 indicates the explained variance from total variance. Thus, it is seen in Figure 7 that at the wind direction I ($R1$), the variation at pollution zone 1 is primarily accounted for by $S1$ $\{(-28.87)^2$ against $(-0.87)^2\}$, pollution zone 2 by $S2$ $\{(11.29)^2$ against $(-3.44)^2\}$, and at direction II ($R2$), pollution zone 1 is mainly affected by $S2$ and there is little difference between $S1$ and $S2$ for pollution zone 2 at this wind direction.

Although the above analysis is very rough, the results are qualitatively consistent with the artificial "physical model." It suggests to us the development of a new method based on these basic ideas where we can include both spatial and temporal variation explicitly in the factor analysis model.

Table 7. Core Matrix

	Frontal Plane, R1		Frontal Plane, R2	
	P1	P2	P1	P2
S1	-28.87	-3.44	2.48	6.84
S2	-0.87	11.29	-14.61	7.29

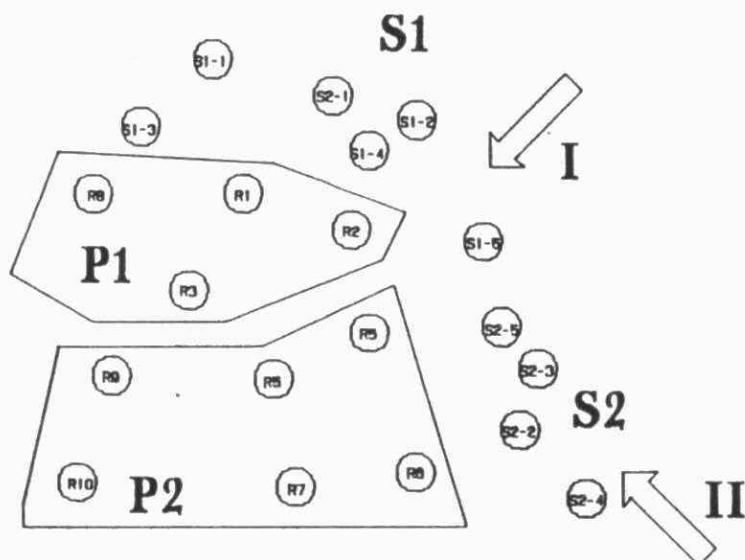


Figure 7. Summary of results of three-mode factor analysis into two source groups (S1, S2), two receptor groups (P1, P2), and two wind direction vectors (I, II).

Future Studies

We are beginning our studies of three-mode factor analysis. In order to apply this method to the APIOS Event Network data, we need to accumulate a data set of composition results over time and locations. In order to simplify our initial efforts, we want to develop a set with no missing data. Thus, there is an effort in progress to extract an appropriate subset of results that will permit us to test three-mode factor analysis for its ability to provide useful insights into the patterns of precipitation compositions obtained by the APIOS Event Network.

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CONTINUOUS MONITORING OF OPACITY, TOTAL HYDROCARBONS AND CARBON MONOXIDE IN AIR EMISSIONS FROM BIOMEDICAL WASTE INCINERATORS. G. Marson, V. Ozvacic, Air Resources Branch, Toronto, Ontario.

New incinerators of biomedical waste in Ontario must be equipped with continuous emission monitors for opacity and total hydrocarbons or carbon monoxide. Purchase of adequate instruments, their installation, operation and maintenance could present difficulties due to high temperatures, corrosive nature of emission gases and the intermittent operation of the incinerators. In order to examine these conditions and to specify appropriate policy guidelines, the Air Resources Branch has undertaken an experimental investigation using commercial instrument packages at two incinerators in Toronto. This paper presents the main findings of the study.

The main conclusion of the study is that useful measurements of the three measured parameters could be obtained on continuous basis, providing proper installation and operation procedures are followed. Opacity readings could be affected by a glow caused by high temperatures, however, the measurement error is small in comparison to opacity levels of concern. No erroneous readings were recorded in the case of total hydrocabons and carbon monoxide.

The instruments were found particularly useful for prompt detection of nonstandard operation of incinerators and the measurements correlated well with process operation and visual emissions.

Development of a Technique for the
Identification of Airborne Particles

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Samples of airborne particulate matter, in some instances, have been found unsuitable for analysis and identification by Xray diffraction because of their size and rate of occurrence. A method of identification using the techniques of electron optics was felt to be a suitable approach for these unknowns, and the purpose of this project was to fully develop the procedure to be followed. The full identification of the nature of airborne particulates is necessary to enable investigators to trace such particles to their source, and reduce or eliminate such sources.

A limitation of such techniques of

electron optics is the thickness of the samples. In transmission electron microscopy a sample thickness the order of 300 microns is suitable, so a technique using an ultra-microtome with a diamond knife was developed. Samples of dust from the plant of a possible source of airborne pollution were obtained for preparation and investigation by this method. Problems which had to be investigated included:

(a) Possible lack of retention of the particles by the mounting medium during slicing of the sample.

(b) The mechanical behaviour of the diamond knife with respect to wear rates and chipping.

(c) Methods of attaining a uniform dispersion of the particles within the mounting resin.

The samples were mounted by first preparing a commercial mounting resin (Araldite), allowing it to harden, then pulverizing it. The unknown samples were mixed with this powder, placed in molds, and liquid mounting resin was added to fill the mold. Vacuum evacuation removed all air bubbles. The sample particles adhered to the surface of the pulverized plastic. This allowed an even dispersion of the particles throughout the mold. After normal preparation

of the samples for microtomy, slices were taken of the required thickness and subjected to electron microscopy. Scanning electron microscopy showed no visible wear to the diamond knife used, and also showed no tendency for the particles to pull out of the mounting resin. The only deleterious effect was a slight loss of the interior portions of the sample particles not originally in contact with the mounting resins.

Subsequent transmission electron microscopy, energy dispersive microanalysis, and selected area electron diffraction allowed identification of the prepared sample, both as to chemical composition, and compound.

The technique was found to be rapid and convenient. A large number of viable samples could be prepared in a short period of time, from a small amount of available sample. Where samples were polycrystalline a rapid identification on the basis of the electron diffraction pattern could be made. Single crystal samples could also be identified, although the procedure is somewhat more tedious in this case.

THE EFFECT OF pH, ALUMINUM, AND DROUGHT ON SUGAR MAPLE SEEDLINGS.

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EXTENDED ABSTRACT

INTRODUCTION

Dieback of sugar maple trees in Ontario, Quebec, and New Brunswick may be linked with air pollution in the form of acid rain. Acidic rain leaches aluminum from soils and converts it to a form that can be toxic to plants. Aluminum interferes with root growth and the uptake of both nutrients and water. Drought, in areas receiving acidic rain, may increase aluminum toxicity and accelerate the death of trees. The purpose of the present study was to determine the effect of acid rain and drought on growth and chemical composition of sugar maple seedlings raised in different rooting media.

METHODS

Seeds were germinated in damp peat moss and were transplanted into soil, sand, or culture solution. In the soil experiment sugar maple seedlings were exposed to 3 drought treatments (wet, normal, dry) and 4 pH treatments (5.5, 4.5, 3.5, 2.5) in a factorial design. In the sand experiment seedlings were exposed to different drought (normal, dry, severe drought); pH (5.5, 4.5, 3.5) and aluminum (0, 20, 100, 250 mg Al/L) stress. In the hydroponic experiment they were exposed to a nutrient solution with and without aluminum, with and without polyethylene glycol (PEG induces water stress). Treatments started one month after plants were transplanted and lasted 4 weeks. Above and below ground biomass as well as symptoms of toxicity were recorded. We then harvested the shoots and roots for chemical analysis (major nutrients and aluminum) using Atomic Absorption Spectrophotometry and Neutron Activation Analysis.

RESULTS AND DISCUSSION

Even though seeds were collected from the same tree, they were highly variable in their response to the different treatments. Plants did not show visual foliar symptoms of aluminum or hydrogen ion toxicity but did have stunted roots in the high aluminum treatments.

Root and shoot chemistry was significantly altered by the treatments. Root aluminum concentrations increased at higher concentrations of treatment aluminum and at lower pHs where aluminum is more soluble (Fig. 1). Aluminum was translocated from roots to shoots, which suggests that foliar aluminum concentrations may reflect edaphic aluminum availability (Fig. 2). The extent to which this occurs in natural soils and in adult trees remains to be determined.

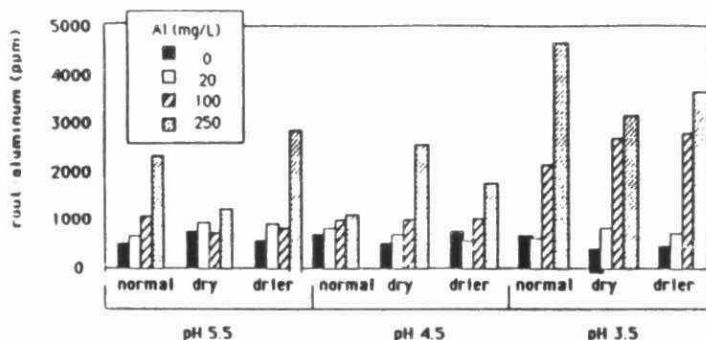


Figure 1. Effect of Al, drought, and pH on root-Al concentrations in sugar maple seedlings grown in sand.

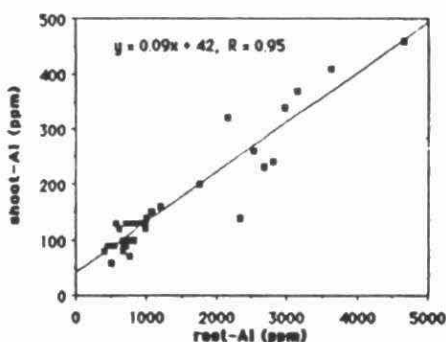


Figure 2. Concentrations of Al in roots and shoots of sugar maple seedlings grown in sand.

Phosphorus concentrations in the roots decreased with increasing drought at pH 5.5, 4.5 and 3.5 (but not at pH 2.5), and decreased slightly with decreasing pHs (Fig. 3). Reduced concentrations of root phosphorus may be the first sign of an aluminum-induced phosphorus deficiency since aluminum is known to precipitate phosphate and thus reduce the amount available for plant uptake.

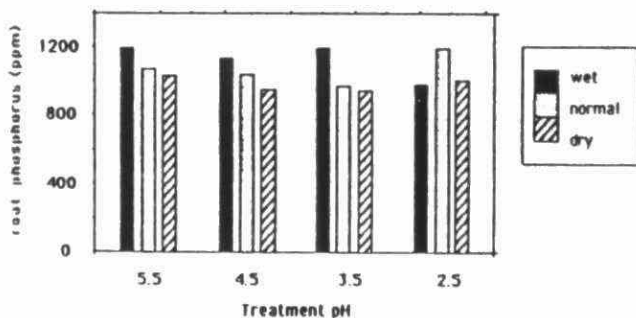


Figure 3. Concentrations of P in roots of sugar maple seedlings grown in soil and exposed to low pH and drought.

One unexpected result was the effect of treatment Al and pH on root sodium concentrations. Root sodium concentrations increased with root aluminum concentrations at pH 5.5 and pH 4.5 (Fig. 4). This response of higher sodium concentrations could be an artifact of our experiment or it could reflect the effects of aluminum and pH on sodium regulation in sugar maple seedlings. If this result is not an experimental artifact, it suggests that acid rain may predispose sugar maple to salt stress which may be a problem along roads.

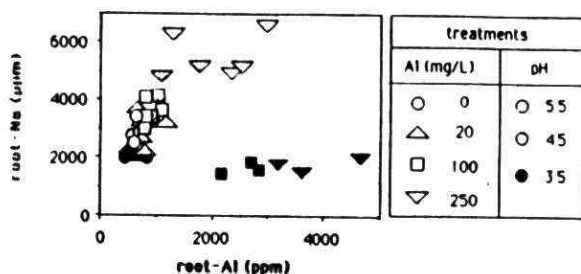


Figure 4. Aluminum and sodium concentrations in roots of sugar maple seedlings exposed to high concentrations of aluminum and low pH.

We had difficulty controlling "drought" in our sand and soil experiments and decided to induce drought physiologically using PEG in a nutrient solution. This experiment is still in progress.

CONCLUSIONS

Sugar maple seedlings were highly variable in their response to drought, aluminum, and low pH. Seedlings did not demonstrate gross visual symptoms of toxicity but did show subtle chemical symptoms of aluminum stress. These symptoms included elevated concentrations of aluminum and reduced concentrations of phosphorus in both roots and shoots. There was also some evidence that aluminum *may* interfere with sodium regulation in sugar maple seedlings. Foliar concentrations of aluminum may be a good indicator of edaphically available aluminum, although more work is needed on mechanisms of aluminum uptake and aluminum translocation in trees.

ACKNOWLEDGMENTS

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CONCENTRATIONS OF PCDD AND PCDF IN SOIL FROM THE VICINITY
OF A LARGE REFUSE INCINERATOR IN HAMILTON, ONTARIO

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M55 128

Abstract

PCDD and PCDF analysis results for a soil sampling survey in the vicinity of a large municipal refuse incinerator in Ontario are presented. No evidence of soil contamination was detected which could be attributed to atmospheric emissions during the 10-year operation of the incinerator.

Introduction

In 1983, the Phytotoxicology Section, Ontario Ministry of the Environment, was requested to conduct a soil sampling assessment survey in the vicinity of a large municipal refuse incinerator near the western tip on the south shore of Lake Ontario in the City of Hamilton. The incinerator, which began operation in 1973, consists of two boiler units venting through separate flues in a 50.3 m stack. The location of the maximum ground level concentration (c-max) was calculated at 1182 m.

In 1982 and 1983, stack testing for organic emissions, including PCDDs and PCDFs, was conducted. These findings confirmed an average annual PCDD and PCDF stack (both flues) output of 4.3 and 10.5 kg/yr, respectively. Separate average annual emission figures for the T4 to O8 congeners revealed per cent contributions to the total emitted (T4-O8) PCDD and PCDF as follows:

PCDD: T4-51%, P5-30%, H6-10%, H7-6% and O8-3%

PCDF: T4-60%, P5-35%, H6-4%, H7-1% and O8 - <1%

Methods

A. Sampling Procedures

The sampling procedure for PCDDs and PCDFs differed from that used for other inorganic type soil surveys in that the sampling equipment was scrubbed laboratory-clean between each site to ensure that no cross-sample contamination occurred. This was accomplished by washing the sampling equipment with an alconox solution and rinsing it with distilled water. The washing step was repeated until all visible soil residue was removed. This was followed by a rinse with 95% denatured alcohol to completely dry the equipment. To remove any residual trace organics which may have adhered to the chromed surface of the sampling corer, it was then rinsed with 1,1,1-trichloroethane.

To further minimize any possibility of cross-site contamination, all sample locations were assumed to be contaminated relative to their distance from SWARU; accordingly, within the survey area, the sites farthest from SWARU were sampled first, followed by progressively closer locations. The field personnel wore clean disposable plastic gloves at each site so that the soil was never touched by unprotected hands.

A 2-m diameter circular plot was established at each of the 14 sample locations. Actual sample collection from within each plot consisted of 15 to 20 soil plugs 2 cm in diameter and 5 cm in depth, yielding approximately 500 g of soil. The soil was placed in a wide-mouth, amber-coloured glass jar which had been solvent-rinsed in preparation for organic samples. The sample jar lid was foil-lined and secured with tape when sample collection was completed. All filled sample jars were placed in separate plastic bags and stored in an insulated, light-tight cooler until delivery to the MOE dioxin laboratory.

B. Analytical Protocol

As the MOE Dioxin Facility did not have an operational protocol to determine PCDD and PCDF in soil, the samples were analyzed by a private laboratory. This laboratory was tested by the MOE with spiked check soil samples and their performance was found to be satisfactory before they began work on the Hamilton soil samples.

A brief summary of the analytical procedures follows.

The samples were received, ground, weighed, air dried and numbered at the MOE Dioxin laboratory prior to being shipped for analysis. Each sample was Soxhlet extracted using toluene. This was followed by a four step multiple column chromatographic clean-up. Some soil extracts required additional treatment with activated copper and AgNO₃ to remove sulfur. Quantification to the low parts per trillion range was made with gas chromatography/mass spectrometry.

Isomer specific identification was not attempted; rather, total concentrations of five congener groups each of PCDDs and PCDFs were obtained. The congener groups included tetraCDD (T₄CDD), pentaCDD (P₅CDD), hexaCDD (H₆CDD), heptaCDD (H₇CDD) and octaCDD (O₈CDD). Similarly, the PCDF congener groups were tetraCDF (T₄CDF), pentaCDF (P₅CDF), hexaCDF (H₆CDF), heptaCDF (H₇CDF) and octaCDF (O₈CDF).

C. Site Selection

Samples were collected at various distances from the incinerator to determine if a soil contamination gradient was present. All sample sites were fully exposed to aerial deposition and were either sodded or had natural grass and/or sedge cover. No private residential properties were sampled.

Fourteen soil sites were chosen and the sampling was conducted on July 7 and 8, 1983. The locations are illustrated on the attached map.

Two of the 14 sites were urban control locations. These were located 3 to 4 km beyond the calculated maximum ground level concentration of emissions from the incinerator. One additional site was a remote, rural control location selected to reflect the levels of PCDDs and PCDFs in soil not exposed to urban activity.

Results

The results of the soil analyses are summarized in the attached table. The data are in parts per billion (dry weight basis) for each of the five PCDD and PCDF congener groups. The MOE does not have a guideline or any other criterion/objective for PCDDs or PCDFs in soil. The U.S. EPA has used the level of 1.0 ppb for 2,3,7,8-TCDD. This was developed by the Atlanta Center for Disease Control as the level for concern regarding human exposure to the most toxic of the 22 possible tetraCDD isomers. No guidelines of any kind exist for any of the other PCDD or PCDF isomers or congener groups.

All 14 of the soil samples had detectable quantities of at least one of the five PCDD congener groups, whereas eight samples contained detectable levels of one or more PCDF congener groups. Only one site (No. 5-1570 m SSE) had a measurable quantity of tetraCDD in the soil. The concentration at that site was 0.007 ppb T₄CDD.

The highest PCDD concentration was 3.5 ppb octaCDD detected at Site 11, 1260 m SW of the incinerator. However, a similar level of 3.2 ppb octaCDD was found in the soil at one of the urban control sites (No. 8, 5570 m ESE) well remote from the incinerator. The soil at the remote/rural control site which was located at the bottom of a ravine approximately 22 km N of the incinerator, contained 0.810 ppb octaCDD. The levels of the other PCDD and PCDF congener groups in soil from the 11 sites around the incinerator generally were within the range detected

in the urban control soils. There were no apparent concentration gradients for any of the PCDDs or PCDFs when compared with distance or direction relative to the incinerator or when considered in terms of the prevailing wind directions (see map).

The location of the maximum ground level concentration (c-max) for emissions from the incinerator stack is illustrated on the attached map as a circle. The five sample sites closest to the c-max were Nos. 2, 5, 6, 10 and 11. Only two of these sites (Nos. 5 and 11) had detectable levels of more than one PCDD congener group. Neither of these two sites was located in the direction of the prevailing winds, which for the last nine years have blown towards the E, NE and N (in the general direction of Lake Ontario) over 50% of the time. In addition, soil at Site No. 2, which is only 160 m from No. 11, contained less than one tenth the octaCDD concentration and no other PCDDs or PCDFs.

Conclusions

On the basis of the PCDD and PCDF analysis results for the 11 survey area and three control site soil collections, and the absence of any concentration gradient or deposition pattern consistent with either prevailing winds or the location of the calculated maximum ground level concentration, it is concluded that emissions from the operation of the incinerator since 1973 have not accumulated in surface soils in the vicinity of the plant.

POLYCHLORINATED DIBENZODIOXINS AND FURANS IN SOIL* AROUND
A MUNICIPAL REFUSE INCINERATOR IN HAMILTON, JULY 1983

Site No.	Distance & Direction from Incinerator	Site Description	Soil Concentration: ppb**											
			tetra	pentra	PCDD hexa	hepta	octa	Total PCDDs	tetra	pentra	PCDF hexa	hepta	octa	Total PCDFs
13	70 m W	- industrial lawn	nd	nd	nd	0.096	0.110	0.206	0.071	nd	nd	nd	0.009	0.080
6	880 m SE	- hydro R.O.W.	nd	nd	nd	nd	0.120	0.120	0.043	nd	nd	nd	nd	0.043
2	1100 m SW	- municipal park	nd	nd	nd	nd	0.310	0.310	nd	nd	nd	nd	nd	nd
10	1260 m NE	- municipal park	nd	nd	nd	0.150	nd	0.150	nd	nd	nd	nd	nd	nd
11	1260 m SW	- municipal park	nd	0.580	0.170	0.390	3.50	4.64	nd	nd	nd	0.180	nd	0.180
5	1570 m SSE	- municipal park	0.007	nd	nd	0.042	0.140	0.189	nd	nd	nd	nd	nd	nd
4	2020 m SSE	- municipal park	nd	nd	nd	.042	1.30	1.342	nd	nd	nd	nd	0.005	0.005
1	2100 m SW	- undisturbed greenbelt	nd	nd	nd	nd	0.075	0.075	nd	nd	nd	nd	nd	nd
9	2140 m NE	- highway R.O.W.	nd	nd	nd	nd	0.050	0.050	nd	nd	nd	nd	nd	nd
7	2380 m E	- industrial lawn	nd	nd	nd	nd	1.00	1.00	nd	nd	nd	nd	0.033	0.033
3	2480 m SW	- municipal park	nd	nd	nd	0.270	0.690	0.96	nd	nd	nd	0.150	nd	0.150
Urban Control														
12	4450 m SW	- school yard	nd	nd	nd	0.005	0.940	0.945	0.009	0.006	nd	nd	nd	0.015
8	5570 m ESE	- school yard	nd	nd	nd	0.097	3.20	3.297	0.068	nd	nd	nd	0.081	0.149
Remote (Rural) Control														
14	22,000 m N	- undisturbed greenbelt	nd	nd	nd	nd	0.810	0.810	nd	nd	nd	nd	nd	nd
Analytical Detection Limit: ppb			0.003	0.0013	0.0013	0.0013	0.0013		0.0003	0.0013	0.0013	0.0013	0.0008	

* Surface soil (sodded), 0 to 5 cm depth

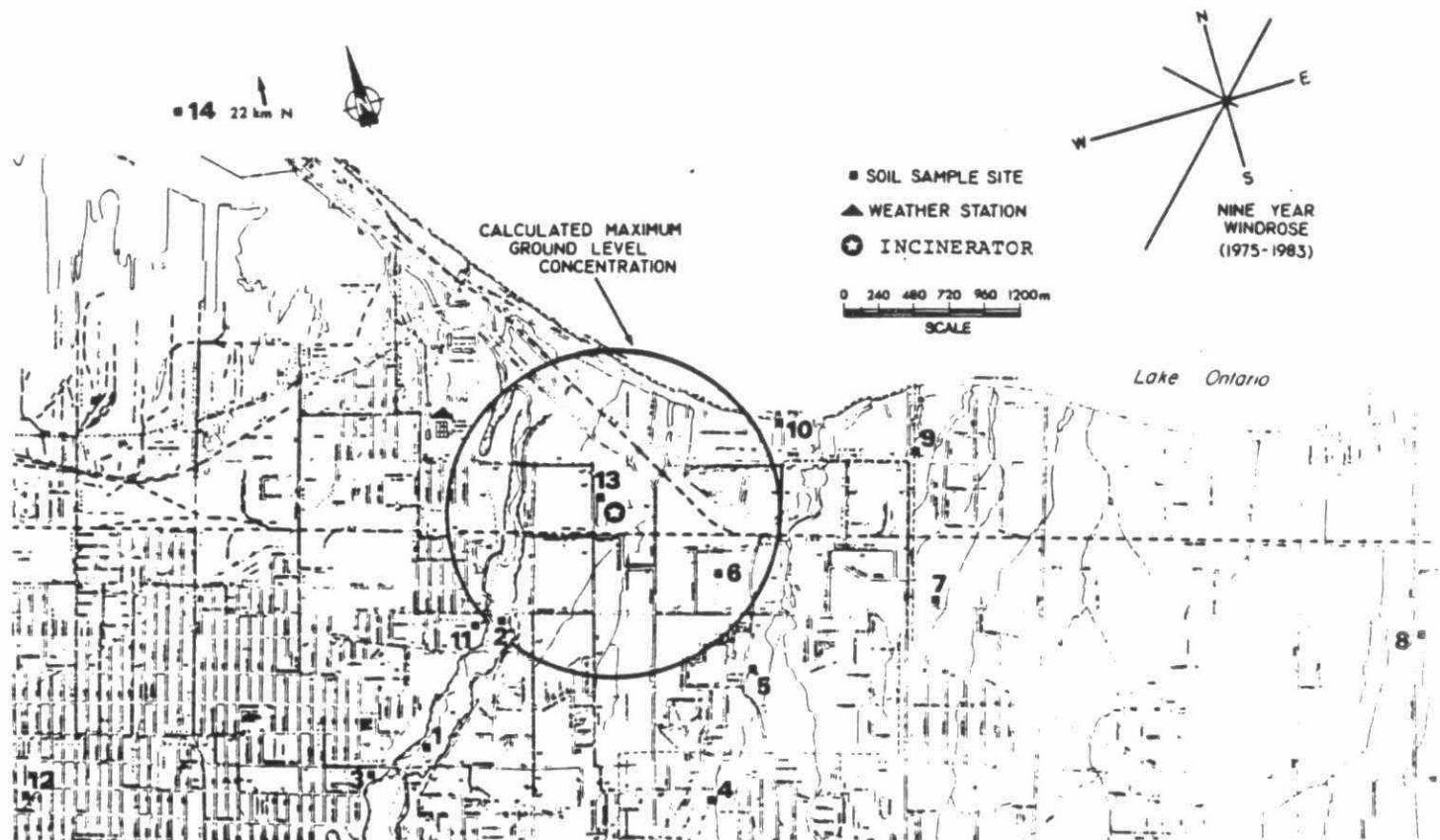
** parts per billion, dry weight

nd Not detected, less than the analytical detection limit

Site No., refer to map.

RE1388-T

LOCATION OF SOIL SAMPLE SITES



DOSE RESPONSE FOR SELECTED ENVIRONMENTAL AIR POLLUTANTS:
A STUDY ON RUNNERS

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Ontario Ministry of The Environment
Project #219RR

INTRODUCTION

People running in an urban environment may be at greater risk to adverse health effects of inhaled pollutants since their ventilatory rate is increased, thus increasing the dose of pollutants that they are exposed to. Furthermore, when they are running alongside busy traffic routes, as is often the case, the concentration of pollutants, such as carbon monoxide can be high. The pollutant load that the runner is exposed to is also affected by exercise intensity (thus respiratory ventilation rate). Exposure is also exacerbated by the fact that at these higher ventilatory rates they often breathe through the mouth, bypassing the normal filtration mechanism of the nose. This study examines health effects of air pollution on runners during training runs in downtown Toronto over a three year period, 1986 - 1988.

OBJECTIVES

Data from three run seasons (April - October) will be evaluated: 1) for differences between central stationary and mobile (personal samplers carried on bicycles following the runners) assessments of pollutant exposure, 2) for the relationship between pollutant exposure during runs and changes in pulmonary function, carboxyhaemoglobin, and symptom reports, separately for each of the above monitoring "networks" with control of wind velocity, thermal load (wet bulb, dry bulb, radiant temperature, combined as WBGT of Minard) and water deficit of atmosphere as covariates, 3) relating sensitivity to pollutants as measured by multiple regression coefficients

obtained above in (2) to general health effects such as sick days and symptoms.

METHODS

Subjects are selected from the Longboat Roadrunners club which carries out weekly training runs covering an area in downtown Toronto and along the Lakeshore corridor during rush hour. There are two groups of runners, a 10 km and 17 km group. Both groups follow the same 8.5 km route, starting and ending at a downtown Toronto site (University Settlement House), although the 10 km group only runs 5 km along the route then returns, while the 17 km group continues to 8.5 km then returns. Pulmonary function (forced vital capacity, forced expiratory volume in one second, peak expiratory flow rate, inspiratory capacity and forced expiratory flow at 50% and 75% of forced vital capacity), and an oxygen rebreathing estimate of carboxyhaemoglobin concentration are measured before and after training runs; individual performance, subject evaluations, respiratory symptomatology and other health/illness information are also obtained.

Pollutant measurements for each run include sulphur dioxide (SO_2), nitrogen dioxide (NO_2), nitric oxide (NO), carbon monoxide (CO), ozone and suspended particulate matter, along with environmental covariates (temperature, humidity, wind velocity and direction). Existing Ministry of The Environment (MOE) air pollution monitoring network data at a central Toronto site (Breadalbane, central MOE) is supplemented by portable

multipollutant samplers (for SO_2 , NO_2 and respirable suspended particulate matter (RSP)). The portable samplers, designed and developed at the Gage Research Institute, use a glass and teflon impinger system with appropriate absorbing solutions for NO_2 and SO_2 , described previously¹. Respirable particulates (less than 10 μm) are collected on a 37 mm diameter Fluoropore filter with a 1.0 micron pore size, using a nylon cyclone (10 mm inside diameter, 10 cm length) at a flow rate of 1.7 l/min. Both NO_2 , SO_2 and RSP concentrations are reported as a time-weighted average over the sampling period. Gage samplers are placed at the central MOE station (stationary samplers), and are carried on bicycles following the runners (mobile personal samplers). There are two bicycles, one bike follows the 10 km group of runners while the other bike follows the 17 km group of runners; both bicycles carry continuous electrochemical CO monitors (Industrial Scientific Devices, model CO-260), readings being taken at specific sites along the route; the 17 km bike also carries a temperature/humidity sampler (Jenway, model 5500), readings being taken at four points along the route.

PRELIMINARY RESULTS

Preliminary results from the first year of the study show a trend towards higher time-weighted average SO_2 , CO and RSP concentrations over the 10 km route, compared to the 17 km route; NO_2 concentrations were similar for both routes. A probable explanation is that the 17 km route extends out along the Martin-Goodman bike/jogging trail, between Lake Ontario and Lakeshore

boulevard. Traffic is lighter and less congested here compared to the downtown core, also it is more open (parkland with few buildings) and offshore breezes may "clean" the area. Furthermore, the 17 km running group returns to the downtown core approximately 1/2 hour later than the 10 km group, when rush hour traffic is reduced and pollution concentrations are lower as suggested by lower CO concentrations. Therefore the runners jogging along the 10 km route, who spend more of their time in the downtown core compared to the 17 km group, may be exposed to higher pollution concentrations (SO_2 , CO and RSP), although the pollutant dose may be similar for the two groups as the 17 km group is exposed for a longer period of time. In addition to our original objectives, it will be interesting to examine whether there are any differences between the 10 km and 17 km group of runners with respect to health effects of air pollution exposure during training runs.

ACKNOWLEDGEMENTS

The support of the Ontario Ministry of The Environment is greatly appreciated (through both its grant program and the assistance and cooperation of its staff). We also acknowledge the excellent cooperation of the Longboat Roadrunners club and the time and effort spent by the staff of the Gage Research Institute.

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STUDY TO DETERMINE THE PHYTOTOXICITY OF
CALCIUM MAGNESIUM ACETATE (CMA) ON FRUIT TREES
AND ORCHARD SOILS IN THE NIAGARA PENINSULA.

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Introduction

At the request of the Ontario Ministry of Transportation and Communications (M.T.C.), the Phytotoxicology Section of the Ministry of the Environment (M.O.E.) was invited to conduct environmental studies relating to the test application of calcium magnesium acetate (CMA) on the Queen Elizabeth Way in the Niagara Peninsula.

The CMA test section was located within M.T.C. District 4, Burlington, at patrol 13, Winona - between interchanges 68 and 64 (Regional Roads 14 and 18) - a distance of 3.9 km. The actual CMA application section within the test zone consisted of 2.4 km portions of both the eastbound and westbound QEW (including service roads and bridge overpasses).

Immediately east of the CMA test section, M.T.C. established a salt control zone. In this zone, the amount of salt applied and its efficacy during the study period was to be closely monitored in order to provide comparative data with the CMA section.

The weather station located at the Vineland Research Station provided valuable meteorological data for coordination with M.T.C. observational results.

Because the CMA and salt test sections were located in the Winona area, a great deal of the 3.9 kilometre treatment zone is bounded by fruit and grape orchards. In previous years, the effects of road salt on many of the fruit tree species located along the QEW has been investigated and documented by the Ministry of the Environment. Therefore, the availability of a variety of fruit tree species for comparative study under the influence of CMA was considered ideal.

Phytotoxicology Study Outline

In addition to studying the phytotoxic effects of CMA on the environment (fruit trees and soils), it was deemed both necessary and important to relate the effects to those induced by road salt. Therefore, the Phytotoxicology study was conceived to examine, not only the effects of CMA but also how those effects compare with those induced by salt.

The final selection of the Phytotoxicology study locations was tempered by predetermined study criteria. In addition to studying the effects of CMA on fruit tree twigs, the effects of the chemical on orchard soils was also to be examined. Finally, a comprehensive network of moss bags would be constructed to determine the comparative airborne lateral mobility of CMA with that of salt from the highway.

The major emphasis of the Phytotoxicology study was intended to be centered within the selected orchard sites. Where possible, sites chosen within the CMA test zone were located on both the south and north sides of the QEW (immediately across from each other if possible) and had a similar composition and configuration of fruit tree species,.

A total of 7 orchard sites were selected for participation in the Phytotoxicology study. Three sites were located within the actual CMA test zone - two on the south side of the QEW and one on the north side. Two sites were selected south of the QEW in a salt zone immediately west of the CMA test zone. Two other sites in the MTC east salt control zone also were selected - one on the south side and the other on the north side of the highway.

A network consisting of 46 moss bag sites also was constructed. Within each of the 7 orchard sites, bags were placed in a line perpendicular to and at increasing distance from the QEW. Moss bags were also placed approximately 0.3 km apart along the service roads on both the north and south side of the highway receiving the CMA treatment.

Twig Evaluation Program

Prior to the selection of each of the 7 orchard sites, an inventory of fruit tree species and their position within the orchard was documented. The 7 selected study orchards were composed of similar species, varieties and arranged in a similar fashion within the properties. The distance of each row and species was measured both from the service roads and from the QEW so that study trees at all 7 sites would be at comparable distances.

At selected distances within each orchard two healthy trees of the same species and variety were selected for twig observation, evaluation and subsequent sampling for chemical analysis. Ten healthy twigs (1986 wood only) on each tree were tagged for evaluation in the summer of 1987 following the winter application of CMA during the 1986-87 winter period. Prior to the first application of CMA or salt on the highway, a replicate sample of healthy twigs (1986 wood only) was excised from each of the two study trees at each position for chemical analysis.

Healthy twigs sampled prior to the application of the CMA have been submitted to the M.O.E. Inorganic Trace Contaminants laboratory in Toronto for the determination of calcium, magnesium, sodium, chloride, lead and iron values.

Twigs which were tagged and exposed to the potential effects of CMA and salt during the winter were excised in early June of 1987. Twigs

were transported to the M.O.E. laboratory in Brampton for measurement and injury evaluation. The length of the 1986 wood of each twig was measured. Twig injury assessed as being induced by 'chemicals' was also recorded. The number of fruit produced by each twig was noted. Following the measurement and evaluation procedure, leaves and fruit were removed and only the twigs were submitted for chemical analysis.

Soil Testing

At the base of each replicate study tree in the 7 orchards sites, 0-5 cm and 5-10 cm soil depths were sampled before and after the application of CMA and salt.

At the time of collection, all soils sampled were classified according to soil type and then submitted to the Ministry laboratory for calcium, magnesium, sodium, chloride, lead and iron analysis. A portion of each sample was dispatched to the Ministry's soil laboratory in Dorset for specialized analysis of available elements.

Moss Bag Monitoring Network

The Phytotoxicology Section has successfully utilized moss bags to monitor airborne elements such as salts and heavy metals. Several years ago, one such study was able to determine the vertical and lateral mobility of road salt along the QEW. (Report titled 'Effectiveness of Snow Fence Barriers in Reducing Salt Spray Injury to Fruit Orchards Adjacent to the QEW: 1979-1981').

Within each of the 7 orchard sites, moss bags were positioned within the crown of the most westerly of the two study trees on a combination metal and wood post approximately 2.5 metres above the ground.

Along both north and south service roads within the CMA and salt control zone, individual moss bags were established approximately 0.3 km apart to detect any possible cross contamination from one zone to another.

The first group of moss bags were set out on November 21, 1986 and exchanged monthly until the final collection on April 23, 1987. All moss bags were submitted to the Ministry's ITC laboratory for the determination of calcium, magnesium, sodium, chloride, lead and iron values.

Summary

All Phytotoxicology field study objectives related to the environmental impact of CMA on fruit trees and soils were achieved. Data related to the chemical content of soils, twigs and moss bags will be processed within available and will be reported.

Future Plans

Snow, ice and temperature conditions during the winter of 1986-87 were considered to be less severe than normal according to MTC standards. As a result, the Ministry still has more than half of the 200 tons of CMA initially ordered for 1986-87 study. Because of the abnormal winter conditions in 1986-87 and the availability of CMA, MTC has decided to repeat the experiment in the winter 1987-88. The Phytotoxicology Section has agreed to participate in the second study although the study objective details have not been finalized.

RE1477

**ESTABLISHING VEGETATION
ON EROSION-PRONE LANDFILL SLOPES
IN ONTARIO**

By

*Tom W. Hilditch and Christopher P. Hughes **

The erosion of a landfill cover can negatively impact upon its function and longevity. The final cover or cap over any closed landfill should perform a number of functions. Chief among these functions are:

- reduce leachate production by preventing direct rainfall infiltration,
- act as a barrier to nuisance animals such as scavenging birds and mammals,
- reduce the danger of fire breaking out in the refuse, and
- improve the aesthetics of the site by covering and containing the refuse.

Erosion of the landfill slopes can impair one or all of these cap functions resulting in increased maintenance costs and/or more complaints from the public. Negative public perception of landfill closure success ultimately results in increased costs for siting future landfills.

The first year of a three year study has contributed to an understanding of the extent and severity of landfill erosion in Ontario. The aim of the program is to develop an approach to remediate landfill erosion through vegetation management.

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Literature was reviewed and individuals involved in North American landfill research contacted. Approaches to landfill revegetation were identified and assessed.

Each Ontario Ministry of the Environment (MOE) District Office was asked to respond to a questionnaire on landfill erosion and revegetation efforts. Through that survey, details of landfill erosion were obtained and example sites identified. Responses indicated that landfill erosion is considered to be a moderate concern in most Districts. In some cases, it was reported to be a serious concern.

Twenty-six landfills (at least four in each of the six MOE Regions) were field-checked to identify in detail the physical and biological characteristics of each. Landfill sites representing (those found in) a wide geographical range were visited, to investigate the variety of plant species, cover types and revegetation efforts found in each Region. One or more landfills were visited in each of the following MOE Districts:

Cambridge	Owen Sound
Cornwall	Peterborough
Hamilton-Wentworth	Sarnia
Kenora	Sault St. Marie
Kingston	Sudbury
London	Thunder Bay
North Bay	Welland
Ottawa	York-Durham

Twelve of these landfills will be selected for test plot planting of preferred revegetation treatments, to take place during Year Two of the study. The test landfills will be selected on the basis of biological and physical attributes as well as geographical distribution.

Test plot monitoring will commence in Year Two and continue into Year Three to assess the over-winter survival of the selected revegetation treatments.

The Year One project report will include:

- a comparison of the degree of landfill erosion as perceived by MOE District personnel against the degree of erosion observed in the field,
- a summary of revegetation attempts and successes on the landfills visited, and
- preliminary findings on the best-available revegetation techniques.

A manual for the revegetation of landfills across the Province of Ontario will be one of the final products of this project.

EVALUATION OF A HI-VOL DENUDER SORBENT SAMPLING SCHEME FOR MEASUREMENTS OF POLYNUCLEAR AROMATIC HYDROCARBONS

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Increased awareness of the adverse health effects of certain organic substances has catalyzed the need to measure their ambient concentrations for monitoring and, if necessary, control purposes. One such group of substances is Polynuclear Aromatic Hydrocarbons (PAH's). PAH's are products of incomplete combustion and include several chemicals which are known carcinogens or mutagens as well as others which are believed to be benign substances. As part of its organic monitoring program, the Air Resources Branch (ARB) of the Ontario Ministry of Environment (MOE) is investigating a sampling method for PAH's which may eventually become the basis for a sampling network.

Laboratory tests have indicated that a modified high volume (Hi-Vol) sampler would provide samples which accurately reflect the atmospheric levels of PAHs. The recommended sampling train consists of a removable ozone denuder made of bundles of kraft paper tubes (in areas and seasons where ozone concentrations are high), a teflon-coated glass fibre filter and a backup cartridge of XAD-2 sorbent resin. ARB has undertaken a series of field trials to test this sampling method. Three separate sets of experiments were conducted to investigate different aspects of this system.

In all cases, air was sampled for continuous 24 hour periods at flow rates of about 590 litres per minute. All sampler exhausts were vented away from the site to avoid resampling the same air volume. Field blanks accompanied all samples to and from the sites and were analysed at the same time as the samples. Analysis of the samples was accomplished with HRGC/dual FID.

The first experiments, which involved two sets of side by side comparisons, were conducted in Windsor and Hamilton. These were designed to study the reliability and reproducibility of the sampling and analytical methods. A number of simultaneous measurements were taken with two adjacent samplers. Levels of the various species were compared for a number of sampling events. To ensure reproducibility, amounts collected on filters were compared separately from those found on the sorbent.

A breakthrough study was undertaken in Hamilton to ascertain if one resin cartridge was sufficient to capture all of the more volatile PAH's. For these trials, a second cartridge of XAD-2 was placed after the first one, in the Hi-Vol train during sampling and analysed separately for PAH's. Any PAH's found on this backup would indicate that one cartridge did not provide a sufficient quantity of sorbent for the volume of air sampled. These experiments were also conducted in duplicate to minimize the chance of error and provide reliability tests for the modified system.

A side by side comparison of samplers with and without a denuder was performed in Windsor, to test the effectiveness and necessity of the denuder. Comparisons of the amounts of PAH's on the corresponding media from the two samplers. Differences between these amounts would indicate that the PAH's which were already sampled were reacting with Ozone. This would give a distorted distribution of the ambient levels of the various species.

Results of these studies and conclusions concerning the effectiveness of the method will be presented.

EFFECT OF FINE PARTICLES ON RESPIRATORY HEALTH
IN A COHORT OF YOUNG PEOPLE
(Studies during adolescence)

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INTRODUCTION

We have previously reported to this Conference the results of studies we have carried out relating to the air quality of Hamilton, Ontario, and its association with differences in respiratory health of a cohort of schoolchildren (5,6,7). In December, 1986, we presented at this meeting some new evidence of the effects of fine particles of urban aerosol on pulmonary function in our cohort, based on analysis of measurements carried out in 1980, when the mean age of the cohort was 10 yr., a time we refer to as "Period 2" (8).

In the present report, we describe the results of the analysis of data obtained during the 6-year period from 1979 to 1984 inclusive. The children were studied again during 1981, which we refer to as "Period 3", and again in 1983-84 (Period 4). Our objective in this communication is to report whether differences in exposure to suspended particles in the years 1979-1984 were associated with differences in respiratory health in our cohort, as measured in 1983-1984 (Period 4).

Specifically, we wished to answer the following questions:

- 1) Does increased prevalence of symptoms, or the presence of pulmonary function abnormalities, observed in children before the start of smoking, predispose a child to a decrement in pulmonary function after smoking has started?
- 2) Are there adverse environmental factors present during childhood which lead to the development of a decrement in pulmonary function on the start of smoking?
- 3) Are there concurrent environmental factors which appear to interact with cigarette smoking in the development of a decrement in pulmonary function?

METHOD

The methods used in our studies have been published, and reported extensively to this Conference in the Proceedings of previous years (Refs 1-8). Briefly, in the Fall of 1978, we drew a sample of over 3200 children from a randomly sampled group of schools in the elementary school system of the Board of Education of the City of Hamilton, Ontario, the children attending at the grade levels of 2, 3 and 4. At the same time, we set up a number of air quality samplers in the city to measure Total Suspended Particulate (TSP), and the Fine Fraction of suspended particles up to and including 3.3 μ m aerodynamic mass median diameter. TSP was measured using standard HiVol samplers, and FF was measured from the cumulative loading of the last 2 stages and the back-up filter of Andersen 2000 samplers.

Respiratory health of the children was assessed in 1979, 80, and 81 by a questionnaire administered to the parents of the children, as well as by a comprehensive battery of pulmonary function tests carried out in the schools. In 1983-4, the young people were again studied in the schools, and a respiratory health questionnaire was administered to the students themselves, as well as a set of measurements of the Forced Vital Capacity (FVC) pulmonary function test. In addition, assessment of the degree of smoking in the cohort was performed in two ways: the students filled out a confidential questionnaire about their smoking habits, and the level of carbon monoxide in their exhaled air (an indicator of recent tobacco smoking) was measured.

Analysis.

Determination of exposure. For the purposes of this study, it was necessary to determine for each period, an exposure which was as much as possible unique to each child in the study. For practical purposes we chose a time resolution of one month, and a spatial resolution determined by the location of the school the child attended at the time of testing. We then developed a method by which we could estimate monthly exposure on a school by school basis. Using the monthly values obtained for each monitoring site for each variable (TSP, FF) a response surface was calculated which expressed in three dimensional terms (one of concentration; the other two of spatial distribution) an estimate of the distribution of air pollution as a function of the geographical plane of the city.

To calculate an exposure value for a given child, an annual mean was obtained by taking the arithmetic mean of the estimate of monthly values of a given variable for the school location for the month of testing; the 9 months preceding it, and the two months following it.

The yearly average was used because we were looking for long-term or chronic effects both in respiratory symptoms and as indicators of these in pulmonary function, and also because plots of yearly air quality measurements indicated that seasonal cycles repeated within the years.

Associations between environmental and health variables.

Factors present before initiation of smoking.

This part of the analysis seeks to answer the first two research questions. The outcome measure used in each analysis was a pulmonary function variable measured during Period 4 of this study. Since this was a continuously distributed variable, multiple regression techniques were used.

We performed an initial analysis (Stage 1) to reduce the number of variables being considered to a reasonable level, because of the large number of variables examined and also because of the high degree of correlation between some of them. We then examined (Stage 2) the effects of the most important variables when introduced together in a multiple regression equation.

Stage 1.

First, the effect of a number of independent variables measured in Period 2 were assessed. These were:

- a) The presence or absence of a number of the subject's respiratory symptoms,
- b) The presence or absence of maternal cough or smoking,
- c) The occurrence or non-occurrence of early hospitalization of the subject for respiratory illness,
- d) The level of family income.
- e) Exposure to ambient (outdoor) total suspended particulates estimated as annual arithmetic mean of monthly geometric mean.
- f) Exposure to the "Fine Fraction" of ambient suspended particles estimated as annual arithmetic mean of monthly geometric means.

Included in the analysis with each of the above was the presence or absence of self-reported smoking during Period 4.

In addition, in each analysis, to allow for baseline differences in pulmonary function (which may or may not reflect pre-existing pulmonary function abnormality), the estimate in period 2 of the particular pulmonary function variable being used as the outcome measure was included as an independent variable in the multiple regression analysis.

Stage 2.

For the second part of the analysis we selected maternal smoking, day or night cough and wheezing as the most consistently important variables seen in the initial analyses. These three variables were then introduced in stepwise fashion along with levels of air pollution and the presence or absence of reported smoking in further multiple regression analyses. These analyses measure the effect of each independent variable on the particular dependent pulmonary function variable, when the other independent variables are also in the equations. The objective was to judge the relative strengths of the effects.

The whole process was repeated for independent variables measured in Period 3.

Factors present after smoking has begun.

The same 2-stage analysis procedure was carried out once again, but here, the independent variables were those measured during Period 4, when for the most part, those who were smokers in the cohort had already started. In addition, the information on respiratory health and home environment was obtained from a questionnaire administered directly to the student, rather than to the parents, as had been done in Periods 1, 2, and 3.

Statistical analyses were performed using sub-programs in the Statistical Package for the Social Sciences (SPSS). These included descriptive statistics, comparison of sample means, and comparison of observed with expected frequencies. The effect of one or several independent variables on a continuously distributed independent variable was also performed by multiple regression using a sub-program from the same package. Adjustment of level of significance for multiple comparisons was performed by the method of Tukey, in which the conventional level of significance is divided by the number of questions being investigated.

RESULTS

Air Quality.

Figure 1 is a plot of the annual average values of fine fraction measured from 3 different sites in Hamilton, for the years 1979 to 1985 inclusive. The Seneca site is located in a residential area in the upper west "Mountain" part of the city; Bart/Went is the main central monitoring site of the Ontario Ministry of the Environment (OME) in Hamilton, located not far from industry in the downtown lower city area, and North Park is a location also maintained by OME on the "Beach Strip", immediately across Hamilton Harbour to the north of heavy industry. It is of interest to note that, although there are substantial differences in the mean values of each site from year to year, the relationships between sites are maintained:

(North Park > Bart/Went > Seneca)

except for 1982. The presence of a gradient in fine fraction across the city provides us with an independent variable with which we may associate differences in respiratory health in our cohort, which is also distributed across the city.

Smoking.

The degree of smoking in the cohort was much greater than we expected. It appears that smoking begins in our cohort at about age 11, and by age 16, nearly half of the girls, and a quarter of the boys smoke more than 1 cigarette a week. The results of the CO measurements confirmed the validity of the estimate of self-reported smoking behaviour, in that 94% of those persons who classified themselves as non-smokers had exhaled CO no greater than 4 parts per million (ppm), and over 88% of those who said they smoked more than 10 cigarettes per week had exhaled CO more than 4 ppm.

Respiratory Health.

Factors present before initiation of smoking.

For independent variables measured in Period 2 the major effects seen were:

- FEV1/FVC was significantly reduced in females in the presence of wheezing and in males in the presence of maternal smoking.
- FEF75/85 also showed a significant reduction in females in the presence of wheezing.
- Maternal smoking in females was associated with an increase in FEV1, FVC, MEF75, FEF2575 and FEF7585.

d) An increase in suspended particulates was associated with an increase in FVC in females, and with increases in FEV1, FVC, MEF50, and FEF2575 in males.

e) No effect of self-reported smoking was seen in females but a positive association similar to but less than that with TSP was seen in males between the presence of self-reported smoking and with FEV1 and FVC, and also with MEF75 and FEF7585.

f) Exposure to Fine Fraction in Period 2 was associated with highly significant increases in FEV1, FVC, MEF50, and FEF2575 in males, and a smaller and less significant increase in FVC in females.

For independent variables measured during Period 3 the following relationships were noted:

a) In both males and females, wheezing was associated with a reduction in FEV1, FEV1/FVC and FEF2575, and an increase in MET. In females, it was also associated with a reduction in MEF50, MEF75, and FEF7585.

b) Maternal smoking in males was still associated with a reduction in FEV1/FVC, and in females was still associated with increases in various pulmonary function variables.

c) The positive association between particulates and pulmonary function found in Period 2 was less marked in Period 3: In females, a significant lengthening in MET was found, but in males a significant positive association with FEV1 and FVC was observed which was smaller in magnitude than in Period 2.

Concurrent Factors

The third research question was concerned with the effect of concurrent environmental factors that might interact with cigarette smoking, when both independent and dependent variables were measured in Period 4.

For males the major association seen was that of self-reported smoking with an increase in a number of pulmonary function variables, that is: FEV1, FVC, MEF75, and FEF7585.

A positive association was also seen between total suspended particulates and several pulmonary function variables, and the same was found for fine fraction. Negative associations were seen between the presence of wheeze and both FEV1 and FEV1/FVC.

In females, self-reported smoking was associated with a reduction in FEV1/FVC and peak flow. Maternal smoking was associated with positive changes in FVC, FEV1, MEF75, and FEF2575, but the presence of a wheeze was associated with a reduction in FEV1/FVC, MEF50, FEF2575, and an increase in MET.

The presence of a day or night cough was associated with a reduction in MEF75. The level of total suspended particulates was associated with an increase in MET, and no associations were found with fine fraction.

Single associations of current smoking with current respiratory symptoms.

We also analysed the prevalence of respiratory symptoms classified according to smoking behaviour. For both males and females, self-reported smoking had a significant association with a cough during the day or night. In addition, for females only, self-reported smoking had a significant association with current wheezing and also with the occurrence of a chest cough during the most recent respiratory infection.

CONCLUSION

In this study, over a six year period, we have obtained pulmonary function data on a cohort of Canadian adolescents. Over the last two-year period, estimates have been obtained of their smoking habits. The validity and repeatability of these data have been estimated and are found to be within acceptable limits. Concurrently with the pulmonary function study of the children, estimates of the exposure to suspended particulates have been obtained and are reported.

Previous state of respiratory health.

Of the variables which we have measured in these subjects before the start of smoking, the presence of wheezing appeared to be the one which most consistently was associated with decrement in pulmonary function during Period 4. This was especially true for females and in this respect, the finding of a significant interaction between wheezing and smoking in females is of importance. Whether the presence of this particular symptom can be used to identify those at risk of pulmonary function impairment on the initiation of smoking can only be determined however by further followup of this cohort. The presence of a cough in females may be an additional risk factor.

Previous environmental factors.

We could find little evidence that exposure during this study to an increased level of suspended particles (even when expressed as the fine fraction) was associated with any decrement in pulmonary function measured during the last two years reported here (Period 4).

Indeed, we found that there was a positive association between the levels of suspended particles as well as fine fraction and a number of pulmonary function variables in males. Only for MET was there observed a significant association with TSP (but not FF) in females, and this positive association is interpreted as an increase in airflow obstruction. Exposure to the effects of maternal smoking in males prior to Period 4 was associated with a decrement in the FEV1/FVC ratio, a finding not observed in females. These data are consistent with the relationships we have described in our previous study.

Environmental factors concurrent with smoking.

In males, no relationships were seen for maternal smoking reported during the current period of study. A positive association was seen between total suspended particulates and several pulmonary function variables, and the same was found for fine fraction. In females, maternal smoking was associated with positive changes in FVC, FEV1, MEF75, and FEF2575. The level of total suspended particulates was associated with an increase in MET, and no associations were found with fine fraction. Thus the only environmental factor other than smoking itself that showed concurrent negative health effects, was the association in females, of TSP with an increase in the time taken to exhale the middle half of the Forced Vital Capacity (MET).

Effects of smoking.

It was surprising to find after such a short period of smoking that we were able to demonstrate a significant increase in the symptoms of cough in both males and females. In addition, in females only, there was a significance in the prevalence of wheeze, associated with smoking. The increases showed a clear dose-response relationship, and illustrate the damage already caused to the lungs of these young people by cigarettes.

Positive associations.

A positive association was observed between self-reported smoking and pulmonary function but only for males. The interpretation of these data is difficult but is suggestive of some element of pre-selection. Unpublished data from our previous study indicates that those who initiate smoking in this time period had larger lung volumes before the start of smoking at the age of eight than those who have not commenced smoking. These differences were significant only for females. It may well be that in this period when smoking is starting, the opposing effects of a selection factor and of smoking itself may make the finding of any smoking effect difficult. Positive associations were also found between TSP and FF and some pulmonary function variables, primarily in males. We speculate that, in addition to some process of selection, there may be a phenomenon of a "compensatory" response to low level exposure to a pulmonary irritant. As yet we do not have direct evidence that this is the case.

ANNUAL AVERAGE FINE FRACTION

SITES IN HAMILTON, ONTARIO

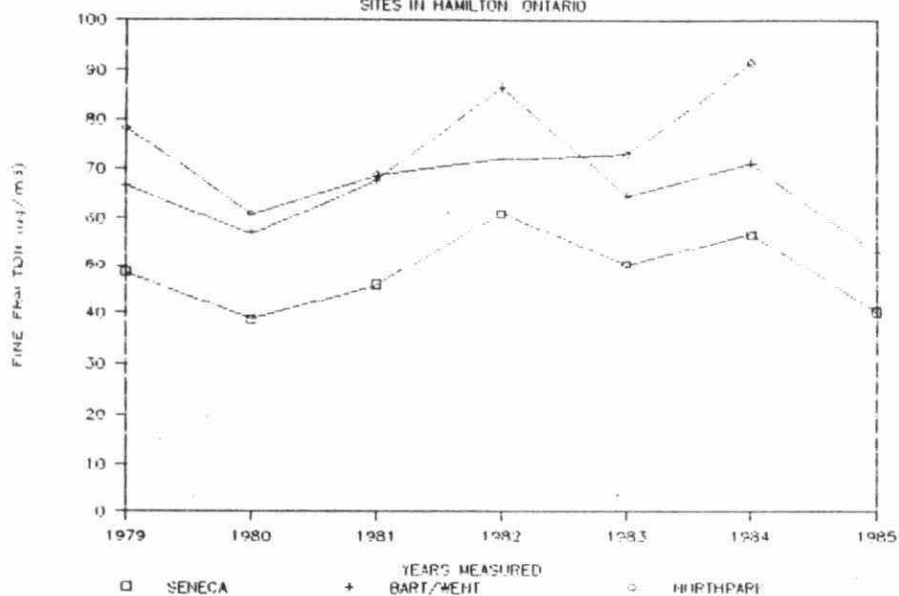


FIGURE 1

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OUTDOOR SOUND LEVEL PREDICTION FOR
INDUSTRY, 1986, Tim Kelsall,* Hatch Associates
Limited, 21 St. Clair Avenue East, Toronto,
Ontario M4T 1L9

Canadian Standard Association Standard Z107.55, Recommended Practice for the Prediction of Sound Levels at a Distance from an Industrial Plant, was published recently. Two tasks associated with this standard were undertaken in the study being reported here.

A software package was prepared which follows the standard and simplifies its use. This should facilitate routine use of the standard.

In addition, the validity of the standard was evaluated by comparison with other predictions and measurements reported in the literature. The standard was found to be slightly less accurate under some conditions than similar European standards, but significantly less complicated.

Verification of the standard on existing plants is recommended as future work.

THE DEPOSITION OF HEAVY METALS AND ACIDITY IN ONTARIO

Neville W. Reid and Maris A. Lysis

ABSTRACT

Trace metal concentrations in air and precipitation are monitored in a network in Ontario, along with concentrations of chemical parameters related to acidity (e.g., pH, sulphate and nitrate). These data have provided the basis for estimates of direct atmospheric input of toxic metals to the Great Lakes. In addition, a special metals monitoring program is under way at one location, including the determination of species such as indium, germanium and arsenic, which are known, or believed, to be tracers for large point sources. Results from this study will assist in the assessment of impacts due to these large sources in acid sensitive areas.

INTRODUCTION

Wet and dry deposition in Ontario are monitored under the auspices of the Acidic Precipitation in Ontario Study (APIOS). Two networks are operated in the province, sampling respectively on one day and twenty eight day cycles. Chemical species associated with atmospheric acidity, such as hydrogen ion, sulphate, nitrate, ammonium, calcium and magnesium are determined in both networks. In addition, a number of metals are determined in the 28 day network. Metals are also determined in a special monitoring program being carried out at Dorset in central Ontario.

Broadly stated, the objectives of the networks are to determine the long term deposition patterns in the province, and also to assist in the identification of the source regions associated with deposited pollutants. The special metals monitoring program is also designed to assist in the identification of sources, by making use of the association of specific tracers with particular sources.

SAMPLING METHODS

In the twenty eight day network precipitation samples are collected using NIC wet-only collectors. Sample collection is into a plastic bag, to ensure that a pristine surface is presented to each sample. Air samples are collected on a three stage filter pack assembly, using a low volume sampling pump (2 litres per minute). Particulate matter is collected on the Whatman 40 front filter, the nylon second filter collects nitric acid, and sulphur dioxide is collected on a pair of Whatman 41 filters impregnated with potassium carbonate in glycerol. The filters are extracted in appropriate aqueous media, and are then analysed as follows. Sulphate, nitrate, chloride, and sulphur dioxide are determined by ion chromatography, ammonium by an automated colourimetric method, and the metals (Na, K, Mg, Ca, Zn, Fe, Ni, Cu, Pb, Al, Cd, Mn, and V) by atomic absorption spectrometry. The same procedures are used for precipitation samples, and further details are provided in the network documentation (ref 1, 2).

For the special metals sampling program, precipitation samples are collected on a daily basis, also into plastic bags, and using a wet-only

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collector. These samples are analysed by inductively coupled plasma/mass spectrometry for Se, V, Mn, Cu, Al, In, As, Sb, B, Ni, Ge, Cd, Pb, and Zn. Air samples are collected, also on a daily basis, on Whatman 41 filters, using high volume air samplers. The filters are analysed by INAA for Se, V, Mn, Cu, Al, In, As, Sb, and Zn.

RESULTS AND DISCUSSION

Deposition patterns for metals have been determined from the twenty eight day network data. Wet deposition is determined directly, while dry deposition is inferred as the product of the measured concentration and a deposition velocity calculated from surface and meteorological parameters. As examples wet deposition patterns for lead and cadmium are shown in Figures 1 and 2. They show the decreasing south to north gradient found for the chemical parameters associated with acidity. This is indicative of the fact that the sources for these metals are predominantly anthropogenic, as is believed to be the case for sulphate.

Patterns of dry deposition are similar, in that they also exhibit a decreasing gradient from south to north, but the levels are somewhat lower. Dry deposition of lead ranges from 60 to 70 grams per hectare per year in the Sarnia-Windsor area to less than 10 grams per hectare per year over much of northern Ontario. This is to be compared with values ranging from over 70 to close to 20 grams per hectare per year for wet deposition. The corresponding ranges for cadmium are from 2 to less than 0.5 grams per hectare per year for wet deposition, with dry deposition being approximately one fourth as large.

Using the deposition estimates derived from network data, it is possible to calculate the loadings of toxic metals presented to the Great Lakes directly by the atmosphere. For example, it has been estimated (ref 3) that direct inputs of lead to Lake Superior are 187 tonne per year by wet deposition and 47 tonne per year by dry deposition. To place these values in context it may be noted that the total inputs were estimated as 241 tonne per year. The atmospheric contribution therefore amounts to approximately 97 % of the total. Estimates for lead and cadmium input to all of the Great Lakes are presented in Table 1.

The daily trace metal data collected in Dorset will be used to help label air parcels according to the source regions which they have traversed. For example, indium has been shown to be a good tracer for non-ferrous metal smelting. Thus, if high concentrations of indium are observed in air or precipitation on a particular day, it may be inferred that the air parcel in question has passed over Sudbury or Noranda. Daily measurements of acidity, sulphate, nitrate, etc. are also made at the same location, so that a direct tie up between source regions and measured concentrations is possible. Similarly, germanium and arsenic are believed to be good tracers for coal combustion, and may be used to estimate impacts due to such sources.

Only preliminary analyses of these daily metals data have so far been carried out. It has been found that precipitation concentrations lie in the range of nanograms to micrograms per litre, with aluminium, lead and zinc typically having the highest concentrations, while indium, germanium and antimony tend to have the lowest concentrations. In air the concentrations are typically nanograms to fractions of a nanogram per cubic metre. The order of the relative abundances is similar to

those found for precipitation samples. For certain of the metals in both air and precipitation there is a strong dependence of concentration on the air parcel sector of origin, reflecting the association of these metals with specific sources.

CONCLUSION

Trace metals are sampled in two programs operated in Ontario. Using these data it has been possible to show that direct input from the atmosphere is the major pathway for the introduction of lead and cadmium into the Great Lakes.

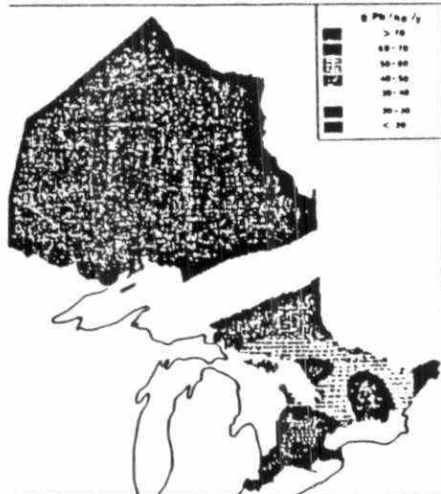
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Table 1

Direct Atmospheric Input of Lead and Cadmium to the Great Lakes

Lake	Lead				Cadmium			
	Wet (t/y)	Dry (t/y)	Wet + Dry (t/y)	Percent of Total	Wet (t/y)	Dry (t/y)	Wet + Dry (t/y)	Percent of Total
Superior	187	47	234	97	6.2	2.4	8.6	69
Michigan	457	83	540	99	9.1	0.8	9.9	78
Huron	318	86	404	98	9.1	0.9	10.0	80
Erie	173	52	225	46	4.3	0.4	4.7	86
Ontario	174	42	216	73	3.5	0.3	3.8	87



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